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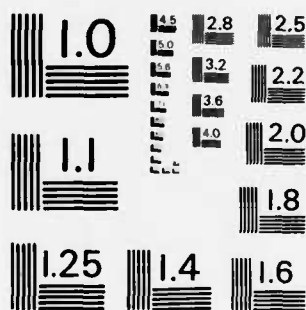
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**SAFETY STUDIES ON LI/SOCI<sub>2</sub> RESERVE BATTERY**

Narayan Doddapaneni  
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104 Rock Road  
Horsham, PA 19044

May 1983

FINAL REPORT for PERIOD 3D SEPTEMBER-1981 - 30 APRIL 1983

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## 20. Abstract

replaced with 1.5M  $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$  electrolyte in the cathode-limited design cells, both the cell discharge life and cell safety improved.

The catalyst stability and stainless steel (bellow material) compatibility were also studied in both neutral and acidic electrolytes. The catalyst was found to be stable and the stainless steel specimens (316L and 321) experienced only surface corrosion after 12-month storage. The surface film formed during the initial surface corrosion appeared to inhibit further corrosion.

Heat cool cycles between  $-40$  and  $71^\circ\text{C}$  of fresh cells and partially or fully discharged D-cells did not adversely influence the cell pressure at the end of 100% depth of discharge. ←

### Acknowledgement

The author acknowledges the experimental assistance of Steven J. Geib and John A. Simmons, and the helpful suggestions of Drs. David L. Chua and Gerald F. Hoff and Mr. Donald Warburton. This work was funded by the U. S. Naval Surface Weapons Center, Silver Spring, Maryland.

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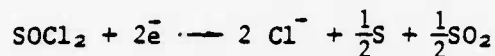


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## 1.0 INTRODUCTION

Safe performance of the lithium-thionyl chloride (1-3) electrochemistry is important if it is to become a viable candidate for potential Navy applications. Some of the safety hazards associated with the system under various conditions have hindered its acceptability despite its many superior performance characteristics. The widely accepted reaction mechanism,



is not fully understood. The intermediate reaction species generated by chemical and electrochemical reactions are not identified fully.

Recent studies (4,5) on electrocatalytic reduction of  $\text{SOCl}_2$  indicate possible reactions involving destabilization of intermediate reduction species via further fast electrochemical reduction and/or modification of the overall reduction mechanism. Thus, at the catalyzed cathode surfaces, the reaction mechanism is simplified resulting in a safer  $\text{Li}/\text{SOCl}_2$  system.

The broad objective of this program is to define, understand, and seek out solutions for the safety problems associated with reserve  $\text{Li}/\text{SOCl}_2$  cells/batteries. Both catalyzed and uncatalyzed cathodes are used in these studies. The two catalysts selected are electrolyte-soluble iron phthalocyanine,  $\text{FePc}$ , and electrolyte-insoluble polymeric cobalt phthalocyanine  $(\text{CoPc})_n$ . Of these,  $\text{FePc}$  has the best catalytic activity for reduction of  $\text{SOCl}_2$  in reserve systems. However, even though  $(\text{CoPc})_n$  has lower catalytic activity than  $\text{FePc}$ , its insolubility makes it a better candidate for active batteries and reserve batteries requiring long discharge life.

Cell design, whether catalyzed or not, is the primary influence on safety of  $\text{Li}/\text{SOCl}_2$  cells/batteries. Both electrode design and electrolyte management are significant factors; specific program objectives were therefore to:

- Determine cell internal pressure characteristics at various discharge depths over a wide range of temperatures. This provides the needed data for vent design at both the cell and battery levels.

- Evaluate long term reservoir storage capability with and without catalyst.
- Evaluate the effect of electrode design (anode-limited vs cathode-limited) on safety during forced overdischarge into reversal, with and without (CoPc)<sub>n</sub> catalyst.
- Elucidate reaction mechanisms and identify intermediate reactive species.

## 2.0 INTERNAL CELL PRESSURE CHARACTERISTICS

Internal cell pressure is one of the uncertain safety factors associated with Li/SOCl<sub>2</sub> systems under a variety of use and abuse conditions, and significantly impacts the design approach for safety vents in Li/SOCl<sub>2</sub> hardware. In the Li/SOCl<sub>2</sub> system, internal cell pressure increases with storage temperature and time, the extent depends upon depth of discharge. Standard D-size cells, equipped with pressure transducers, were used to measure this pressure response. These data can be used to aid in designing safety vents for Li/SOCl<sub>2</sub> reserve batteries. A total of eight cells were built to accomplish this task. Four of these cells contained (CoPc)<sub>n</sub> catalyzed cathodes; the remainder were built with uncatalyzed baseline cathodes.

### CELL COMPONENTS

- Anode

A 0.020" thick lithium foil (Foote Mineral Company) was used, with two pieces sandwiched around a 316L stainless steel current collector. The physical data of the anodes were:

Dimensions:	1.75" x 6" x 0.020"
Area:	135.5 cm <sup>2</sup>
Weight (of lithium):	3.676g
Anode Capacity:	3.676 grams x 3.86 Ah/gram (theoretical) = 14.19 Ah

- Cathode

All cathodes were fabricated via the process described in Figure 1. Baseline cathodes contained 100% compressed-grade Shawinigan acetylene black (SAB) and Teflon-6 binder in a 95/5 weight percent ratio. The (CoPc)<sub>n</sub> catalyzed cathode composition was 90% SAB, 5% catalyst and 5% Teflon-6 binder. Two cathode pads were pressed on either side of a 316L stainless steel current collector.

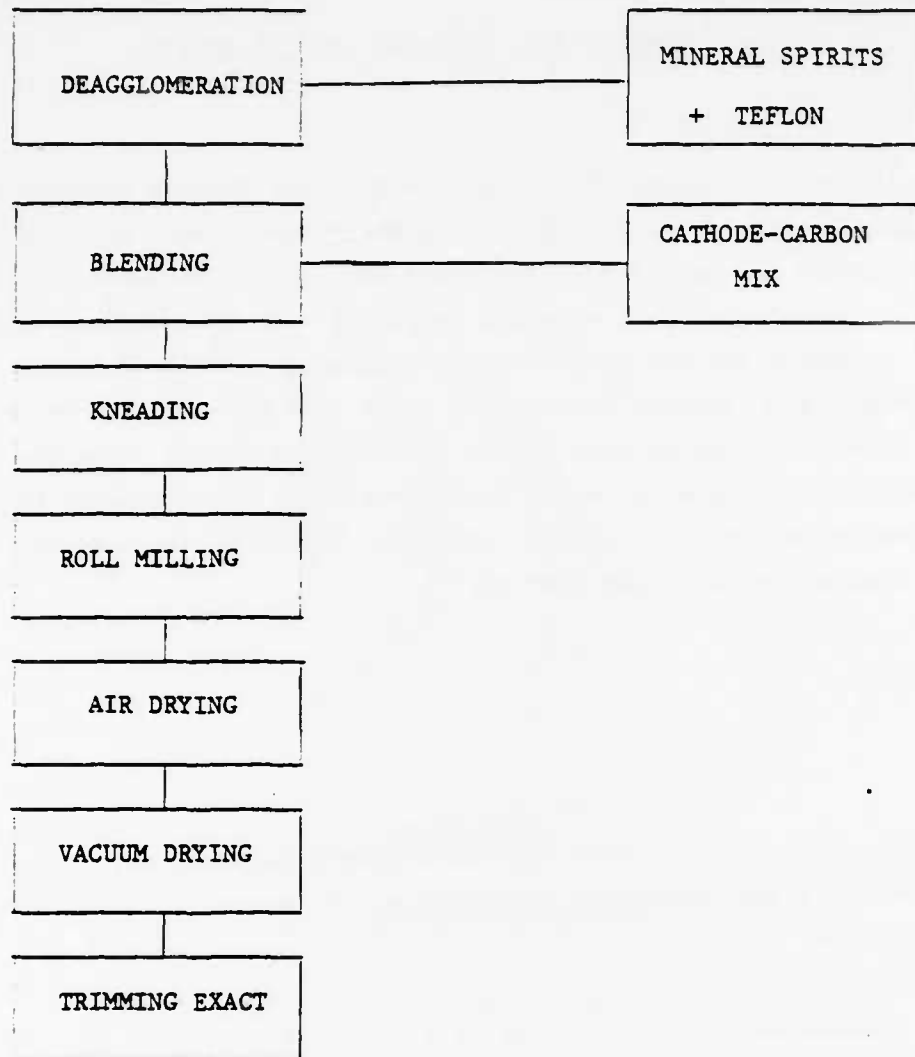


Figure 1. Flow Diagram of Cathode Fabrication Process. Workability of the process not restricted to specific carbon type. Rolling incurs excellent mechanical integrity on the cathode.



The physical characteristics of the cathode pads were:

Dimensions: 1.75" x 8" x 0.040" (one piece)  
1.75" x 9" x 0.040" (second piece)

Baseline Cathode

Total Cathode Area: 192.0 cm<sup>2</sup>  
Total Weight of Cathode: 6.94 g  
Volume: 19.501 ml  
Density: 0.356 g/ml  
Carbon Volume:  $(95 \times 6.94 \div 1.95) \div 100 = 3.381$  ml  
Teflon Volume:  $(5 \times 6.94 \div 2.2) \div 100 = 0.258$  ml  
∴ Total solid volume of cathode:  $3.381 + 0.158 = 3.539$  ml  
Void space in the cathode:  $19.501 - 3.539 = 15.962$  ml  
Porosity:  $(15.962 \div 19.501) \times 100 = 81.85\%$   
Projected Cathode Capacity: 6.94 grams x 1.75 Ah/gram = 12.14 Ah

Catalyzed Cathode

Total Cathode Area: 192.0 cm<sup>2</sup>  
Total Weight of Cathode: 7.31 g  
Cathode Volume: 19.501 ml  
Density: 0.375 g/ml  
Carbon Volume:  $(90 \times 7.32 \div 1.95) \div 100 = 3.374$  ml  
Teflon Volume:  $(5 \times 7.31 \div 2.2) \div 100 = 0.166$  ml  
Catalyst Volume:  $(5 \times 7.31 \div 2.2) \div 100 = 0.116$  ml  
(Catalyst Density estimated to be 2.2 g/ )  
Total Solid Volume:  $3.374 + (0.166 \times 2) = 3.706$  ml  
Void space in the cathode:  $19.501 - 3.706 = 15.795$  ml  
Porosity:  $15.795 \div 19.501 = 81\%$   
Projected Cathode Capacity: 7.31 grams x 2.0 Ah/gram = 14.62 Ah

- Separator Material

Non-woven glass mat separators, manufactured by the Manning Paper Company, were used. The physical data were:

Dimensions:	2" x 11" x 0.005"
Area:	141.94 cm <sup>2</sup> (each side)
Volume:	1.802 ml
Weight:	0.432 g
Porosity:	90%
Solid Volume:	$\frac{1.802 \times 10}{100} = 0.180 \text{ ml}$
Void Space:	1.622 ml

- Current Collector

Stainless steel 316L current collector grids and leads (Lancaster Manf. Co., PA) were used for both anode and cathode. The selection of 316L stainless steel was based on the fact that this same material was being used under Contract N60921-81-C-0351, supported by NSWC.

Anode Grid Dimensions:	1.6" x 5.5" x 0.010"
Weight:	1.318 g
Cathode Grid Dimensions:	1.6" x 7.5" x 0.010"
Weight:	1.688 g
Volume:	1.966 ml
Density of Grid:	$1.688 \div 1.966 = 0.8586 \text{ g/ml}$
Density of 316L SS:	8.00 g/ml
∴ Solid Volume of Grid:	$(0.85686 \times 1.966) \div 8.0 = 0.211 \text{ ml}$
Void Space:	$1.966 - 0.211 = 1.755 \text{ ml}$

• Insulators

Tefzel sheets, 0.005" thick and 1.27" in diameter, were used at both top and bottom of the electrode wrap as insulators. The top insulator had a 0.10" slit slightly off center through which the anode lead passed.

D-cell cans (316L S.S.), terminal plates, grids and leads were cleaned in methyl ethyl ketone (MEK) before use. Leads were spot welded to current collectors, the cathode lead was spot welded to the cell case, the anode lead was spot welded to the center pin, and the cell was closed by laser welding the terminal plate to the cell case.

EFFECT OF INTERMITTENT DISCHARGE ON CELL PRESSURE

Four D-cells, two with baseline cathodes and two with  $(\text{CoPc})_n$  catalyzed cathodes, were activated by vacuum fill technique. In each cell, 28 ml of 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte was added to fill up the void space in the electrode stack. The theoretical capacity of the electrolyte was approximately 21 amp-hours. Thus, the cell was insured of flooded condition throughout its life since the maximum theoretical output of the cell design was 14.2 Ah based on lithium weight.

After activation the cells were allowed to stand at ambient temperature for 6 hours and then they were placed in an environmental chamber built by Tenney Engineering, Inc., New Jersey. This chamber, Model #BTR, was equipped with a programmable memory for heat-cool cycles and a battery backed power to protect the memory in case of electrical failure. For the present study, the chamber was programmed to cool down to  $-40^\circ\text{C}$  from ambient temperature in two hours and then start heat-cool cycles. During these cycles, the temperature was programmed to increase or decrease by  $11^\circ\text{C}$  and come to equilibrium. A total of 45 minutes was allowed for each change in temperature. For each heat-cool cycle between  $-40^\circ$  and  $71^\circ\text{C}$ , a total of 15 hours was required.

Fresh cells were subjected to six heat-cool cycles. A small increase in pressure between  $38^\circ$  and  $71^\circ\text{C}$  was observed after six cycles. However, no hysteresis between pressure and temperature were observed.

These cells were then discharged to approximately 50% depth of discharge at a constant current of 0.192A ( $1 \text{ mA/cm}^2$ ), after which six heat-cool cycles were carried out. In Figures 2 and 3, the relationship between pressure and temperature for the first and the last cycle is shown. It should be noted that the pressure values were not corrected for the void space in the pressure transducer. No significant differences were found between catalyzed and uncatalyzed cells. During heat-cool cycles, the small hysteresis recorded could be attributed to the insufficient time allowed to reach equilibrium temperatures.

After heat-cool cycles, the above cells were further discharged to 0.7 volts and then subjected again to six more heat-cool cycles. In Figures 4 and 5, the pressure-temperature behavior is plotted for the first and sixth cycle. Since the pressure values were not corrected for the extra void space due to pressure transducer and valve, the pressure in an actual D-cell will be higher than reported in Figures 1-5. Actual cell pressure at  $71^\circ\text{C}$  is expected to be approximately 100 psi for both catalyzed and uncatalyzed cells.

The discharge characteristics and the pressure of cells with depth of discharge are plotted in Figure 6 and 7. The cell with the catalyzed cathode showed nearly 150 mV higher voltage than the one with an uncatalyzed cathode. However, the cell life and pressure were not significantly effected by  $(\text{CoPc})_n$  catalyzed cathodes at the low current discharge rate of  $1 \text{ mA/cm}^2$ .

#### EFFECT OF CONTINUOUS DISCHARGE ON CELL PRESSURE

In order to check if any chemical changes took place when the cells were subjected to heat-cool cycles after each depth of discharge, four fresh D-cells were 100% discharged and then were subjected to heat-cool cycles. The discharge characteristics along with the internal pressure of cells with baseline cathodes (two cells) and  $(\text{CoPc})_n$  cathodes (two cells) are given in Figures 8 and 9, respectively. The cell pressures reported in Figures 8 and 9 are the corrected values for the void space due to pressure transducer and the valve attachments. The pressure levels at the end of discharge for this mode of continuous discharges are, for practical purposes, the same as the ones that were intermittently heated and cooled (See Figures 6 and 7).

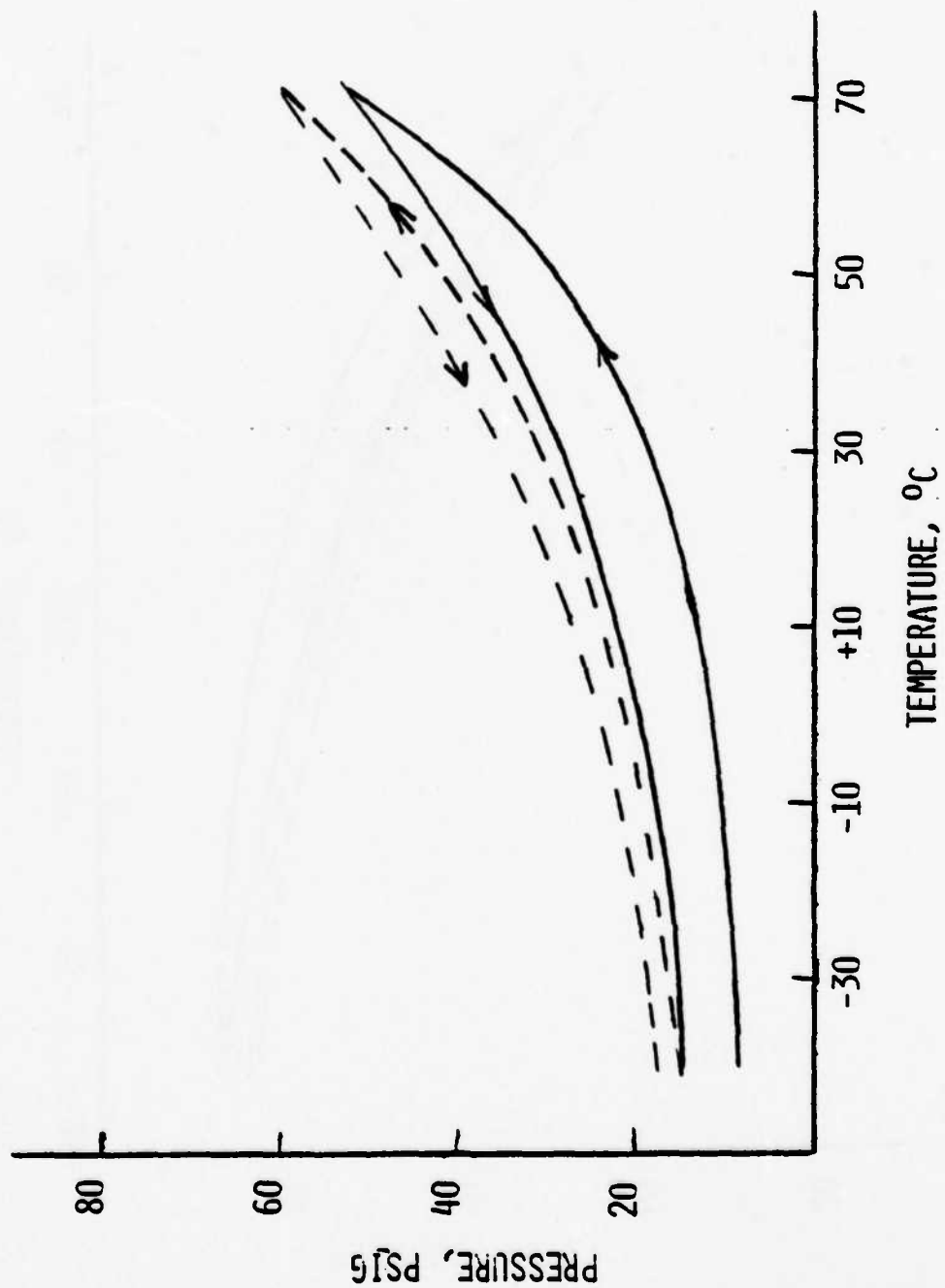


FIGURE 2. HEAT-COOL CYCLES OF L1/SOCl<sub>2</sub> D-CELL WITH 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> ELECTROLYTE AFTER 41% DEPTH OF DISCHARGE. - FIRST CYCLE, ---- SIXTH CYCLE.



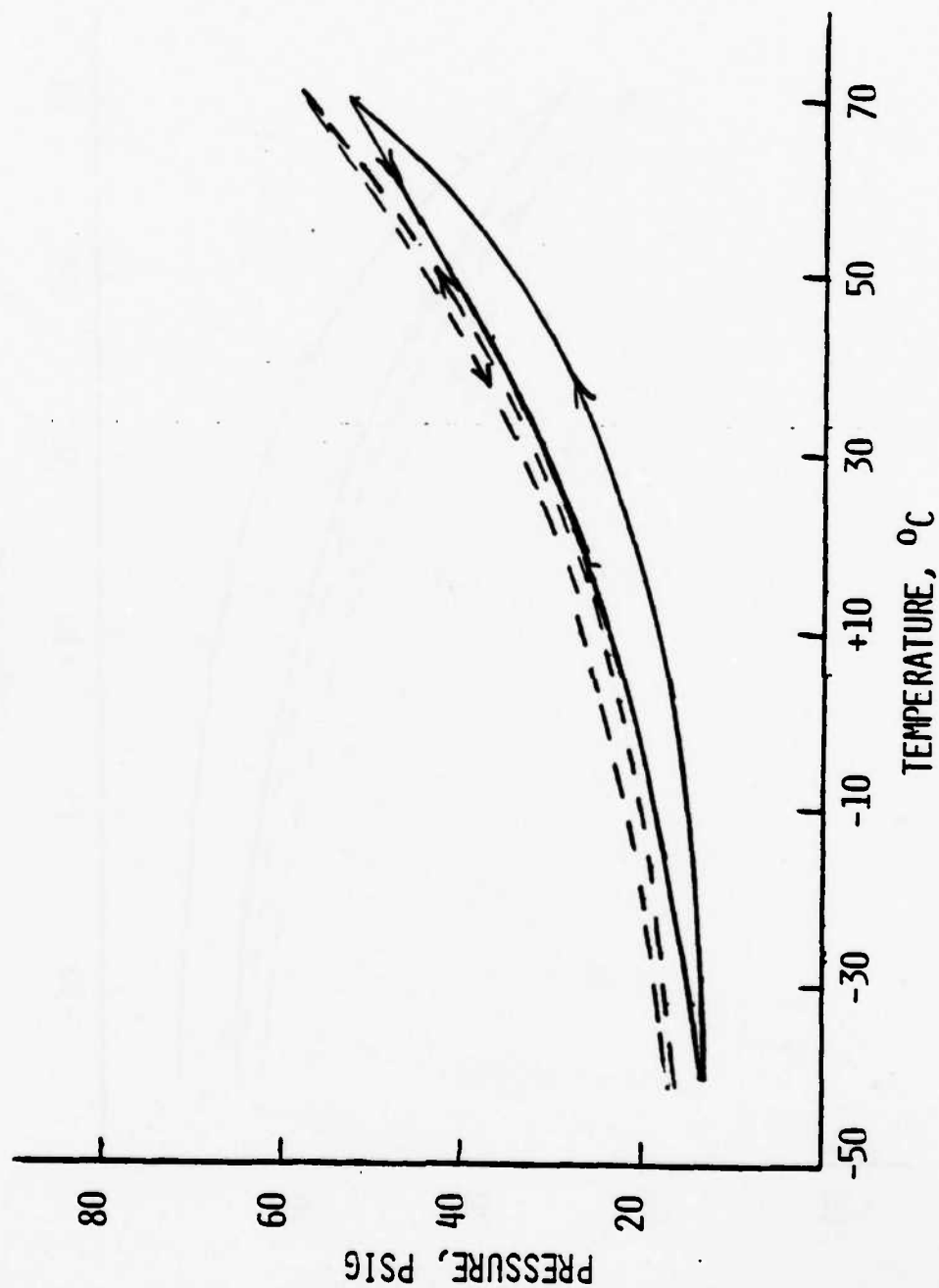


FIGURE 3. HEAT-COOL CYCLES OF  $\text{Li}/\text{SOCl}_2$  D-CELL WITH (CoPc) CATALYZED CATHODE AND 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AFTER 45% DEPTH OF DISCHARGE. - FIRST CYCLE, --- SIXTH CYCLE.

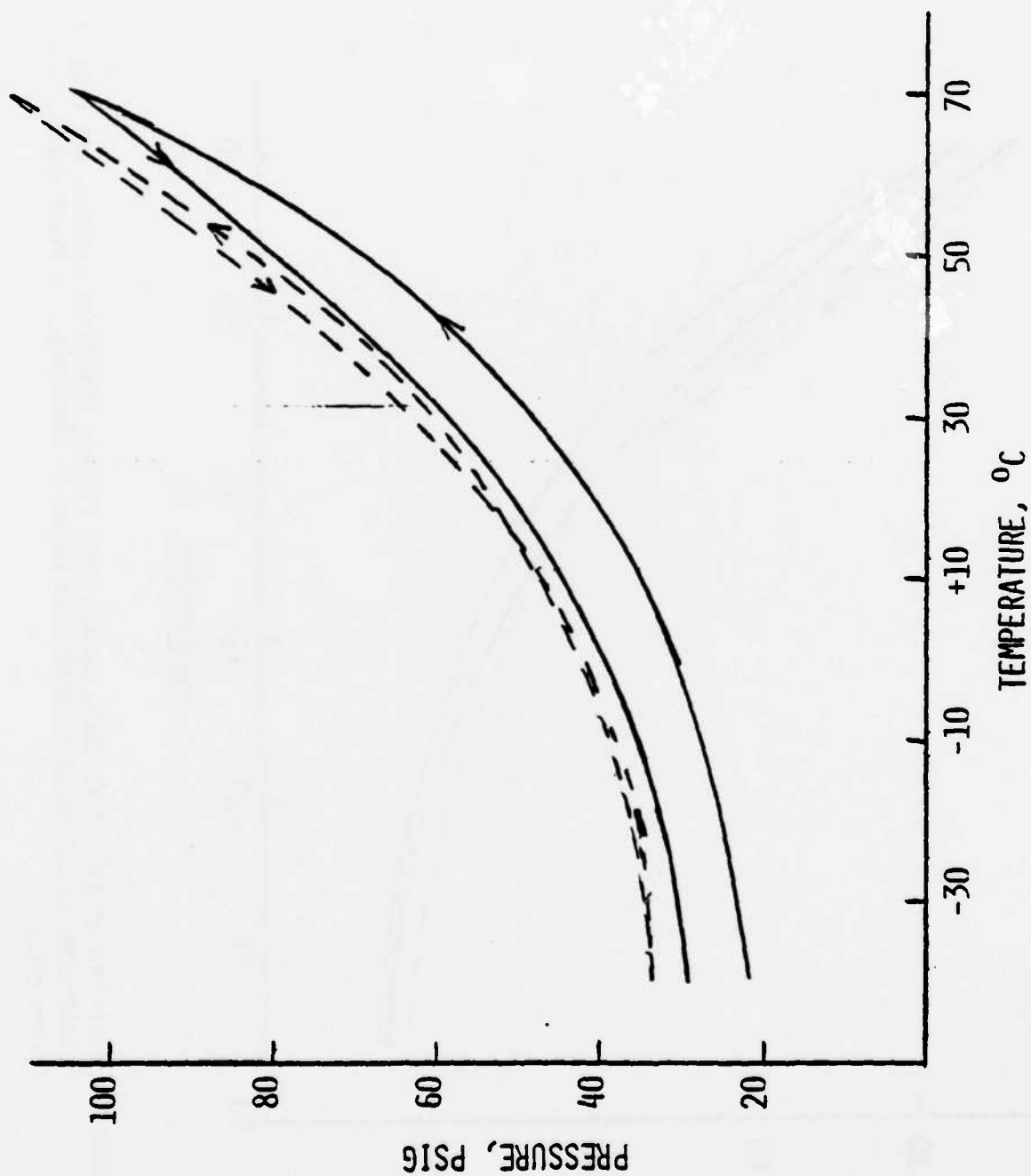


FIGURE 4. HEAT-COOL CYCLES OF  $\text{Li}/\text{SOCl}_2$  D-CELL WITH  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE. - FIRST CYCLE, --- SIXTH CYCLE.

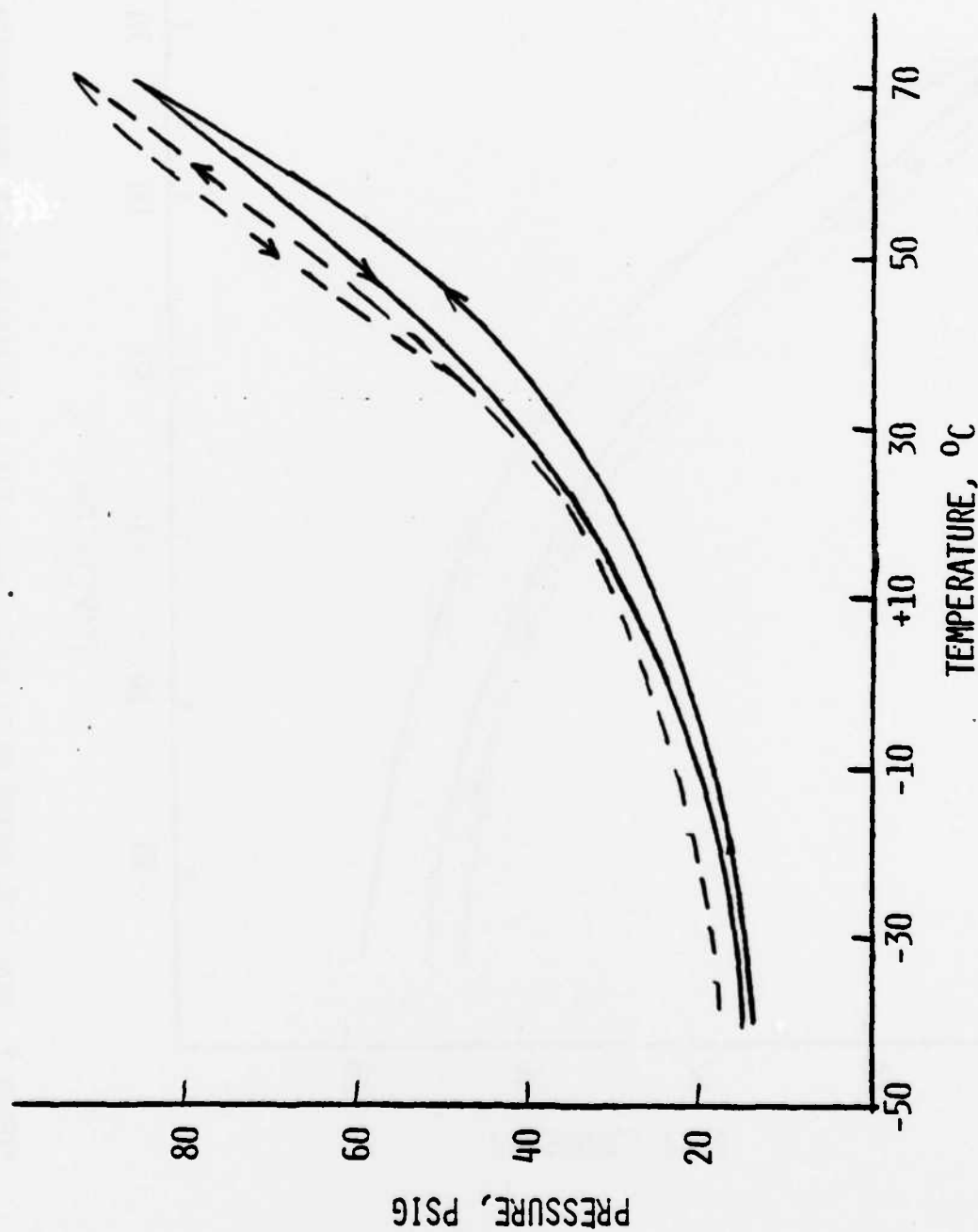


FIGURE 5. HEAT-COOL CYCLES OF  $\text{Li}/\text{SOCl}_2$  D-CELL WITH  $(\text{CoPc})_2$  CATALYZED CATHODE AND 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE. - FIRST CYCLE, --- SIXTH CYCLE

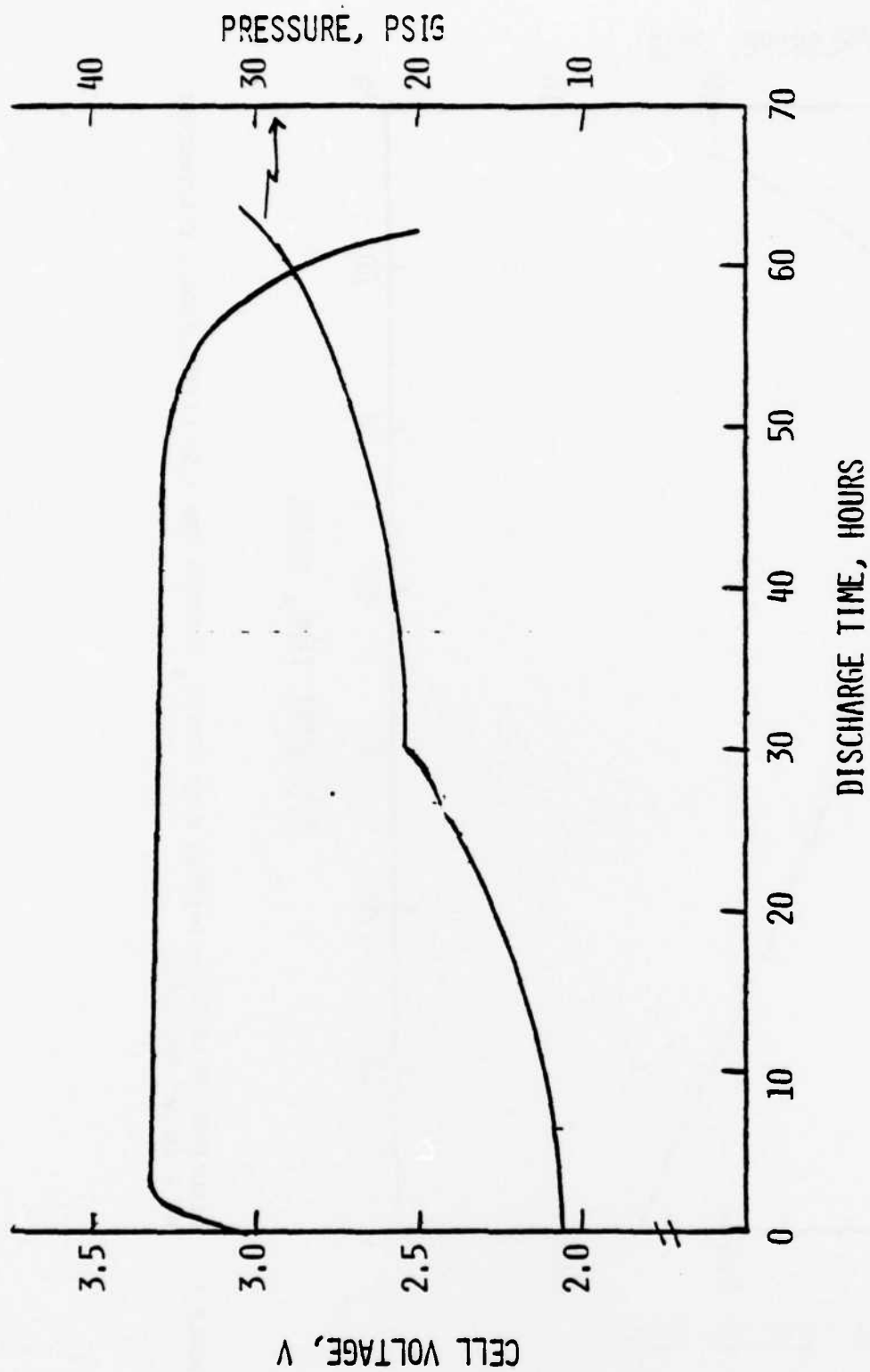


FIGURE 6. DISCHARGE OF  $\text{Li/SOCl}_2$  D-CELLS WITH  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AT  $1\text{ mA/cm}^2$  AND  $23^\circ\text{C}$ .

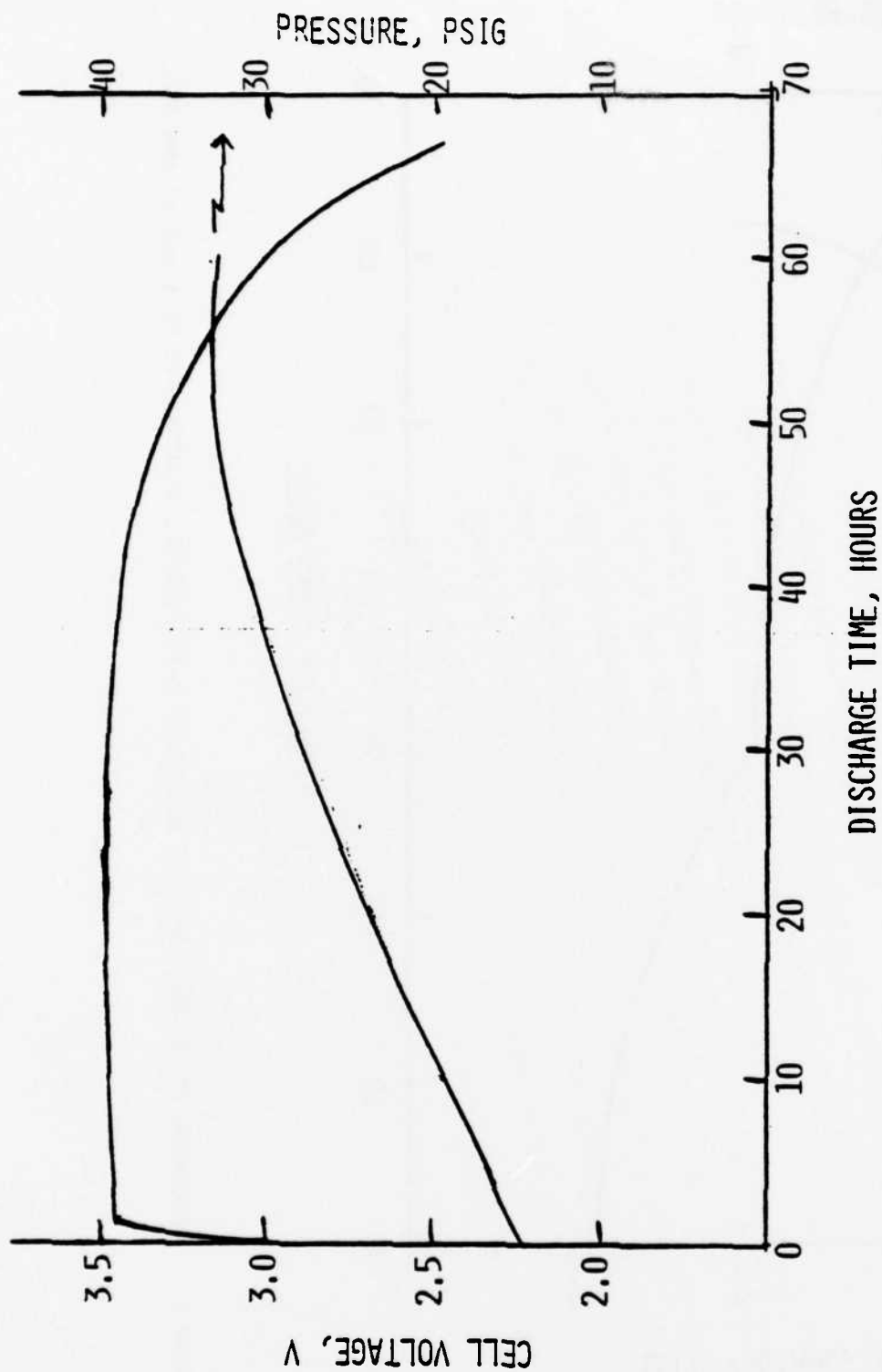


FIGURE 7. DISCHARGE OF  $\text{Li}/\text{SOCl}_2$  D-CELLS WITH  $(\text{CoPc})_n$  CATHODE AND  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AT  $1\text{ mA}/\text{cm}^2$  AND  $23^\circ\text{C}$ .



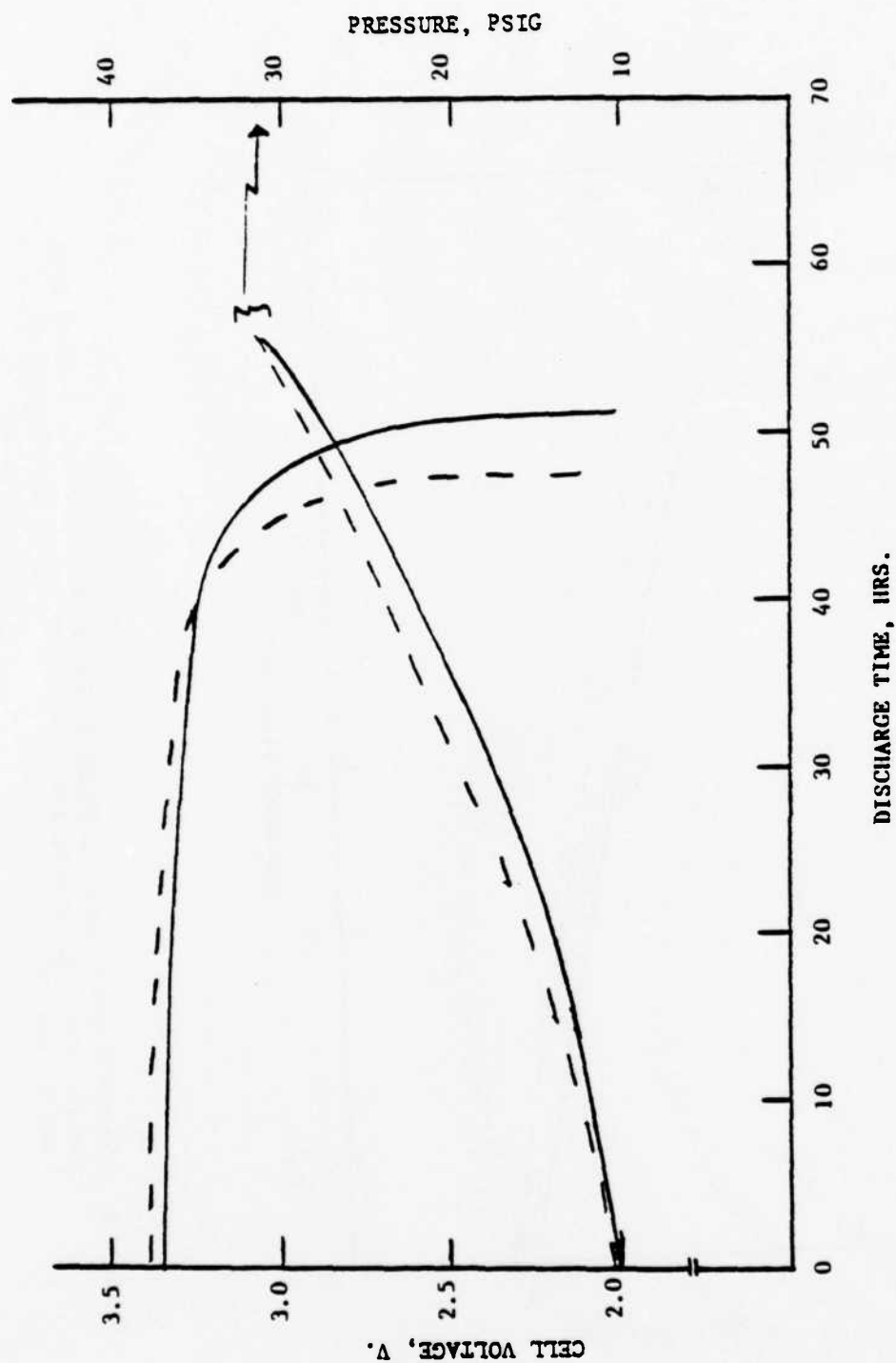


FIGURE 8. DISCHARGE PERFORMANCE AND PRESSURE BEHAVIOR OF  $\text{Li}/\text{SOCl}_2$  D-CELLS WITH POROUS CARBON CATHODE AND  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AT  $1 \text{ mA}/\text{cm}^2$  AND  $23^\circ\text{C}$ .

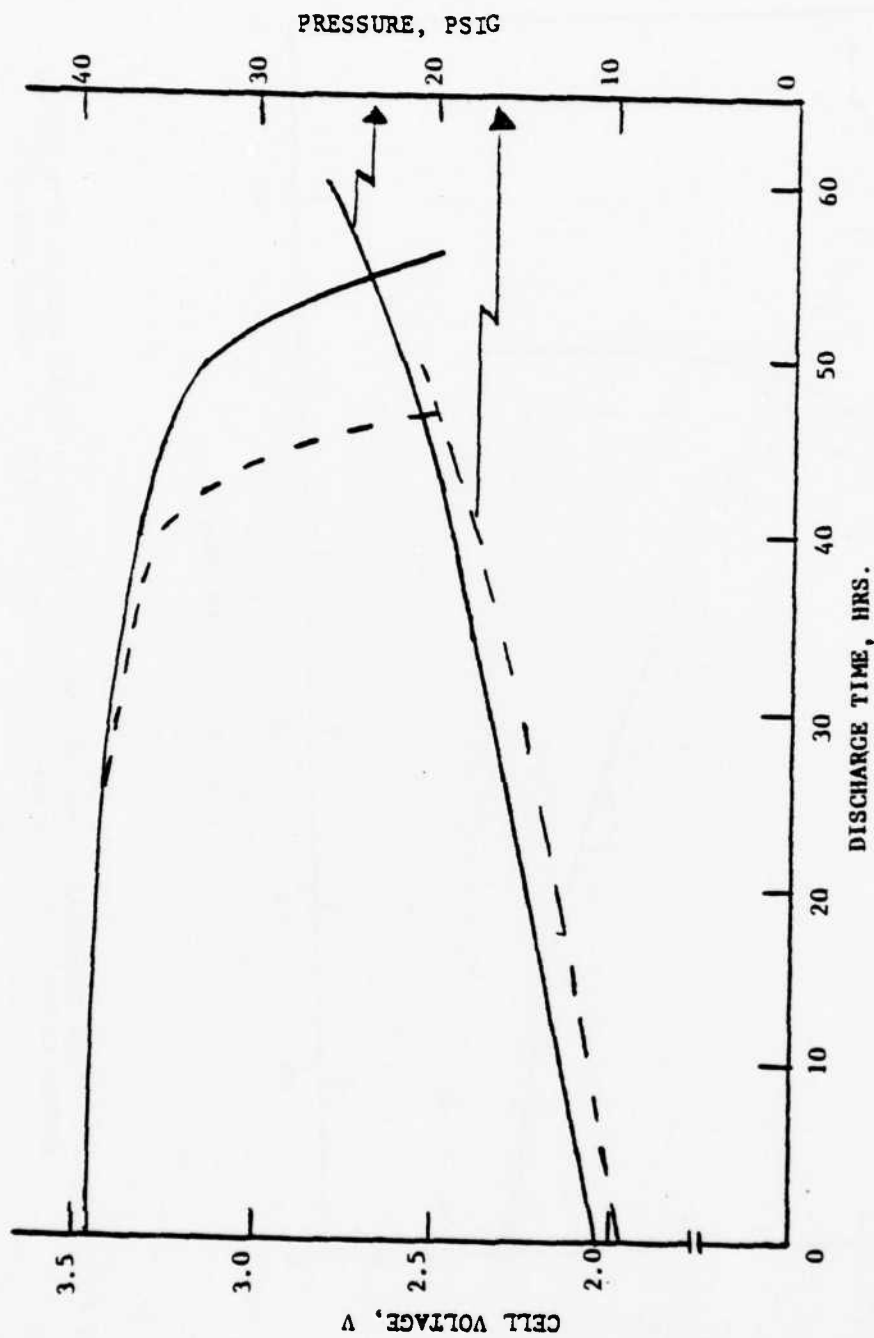


FIGURE 9. DISCHARGE PERFORMANCE AND PRESSURE BEHAVIOR OF L1/SOCl<sub>2</sub> D-CELLS WITH (CoPc)<sub>n</sub> CATALYZED CATHODE AND 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> ELECTROLYTE AT 1 mA/cm<sup>2</sup> AND 23°C.

The four D-cells after 100% depth of discharge were subjected to heat-cool cycles. In Figures 10 and 11, the pressure-temperature hysteresis of these cells are given. Again, no severe deviation was observed from the behavior found in cells which were subjected to several heat-cool cycles at various depths of discharge shown in Figures 4 and 5. The maximum pressure buildup under normal discharge conditions (100% DoD to 0.0 volts) is less than 100 psig.

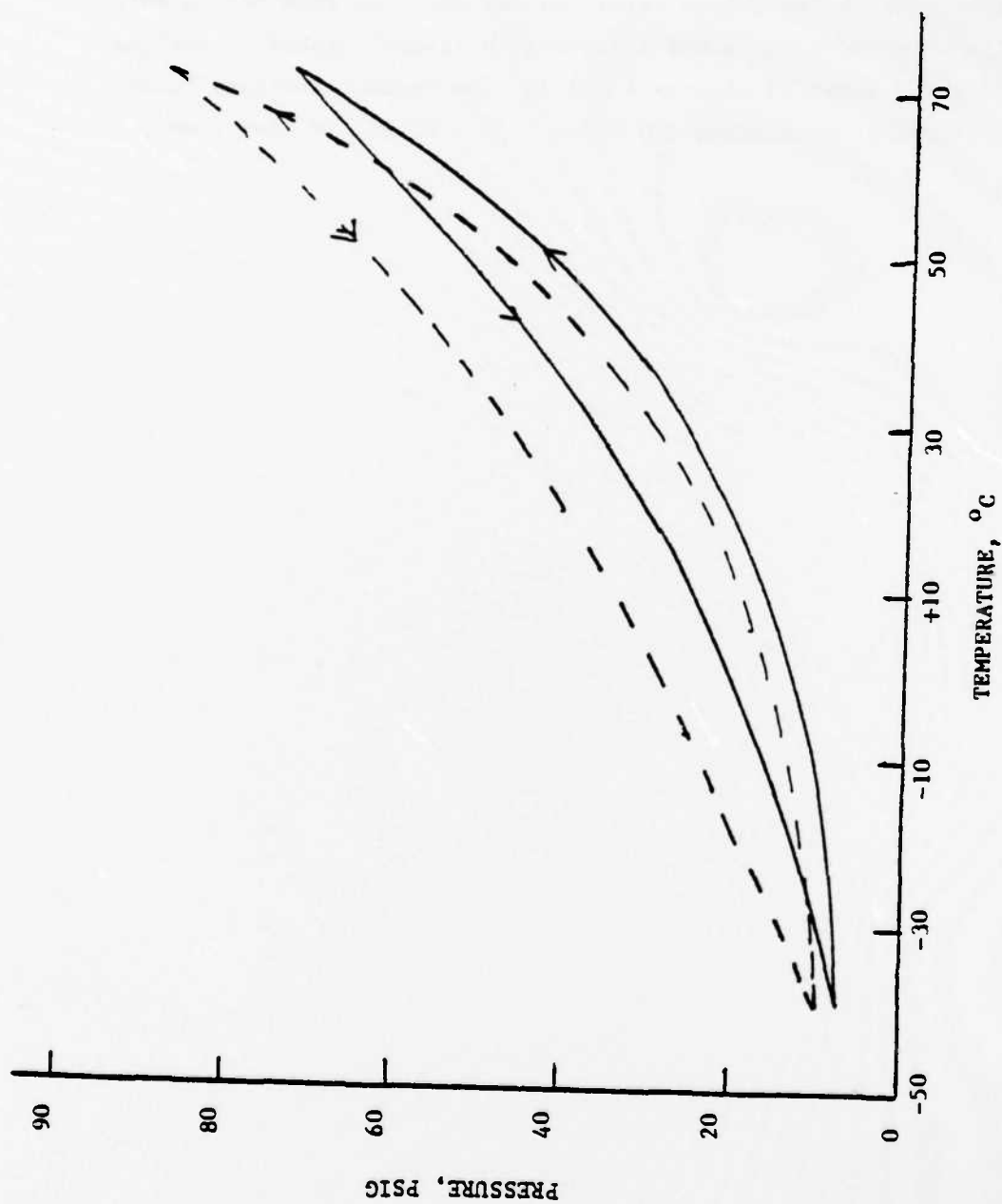


FIGURE 10. HEAT-COOL CYCLES OF  $\text{Li}/\text{SOCl}_2$  D-CELL WITH BASELINE CATHODE AND  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE AT A CONSTANT (CONTINUOUS) DISCHARGE OF  $1 \text{ mA}/\text{cm}^2$ . FIRST CYCLE ---, SIXTH CYCLE

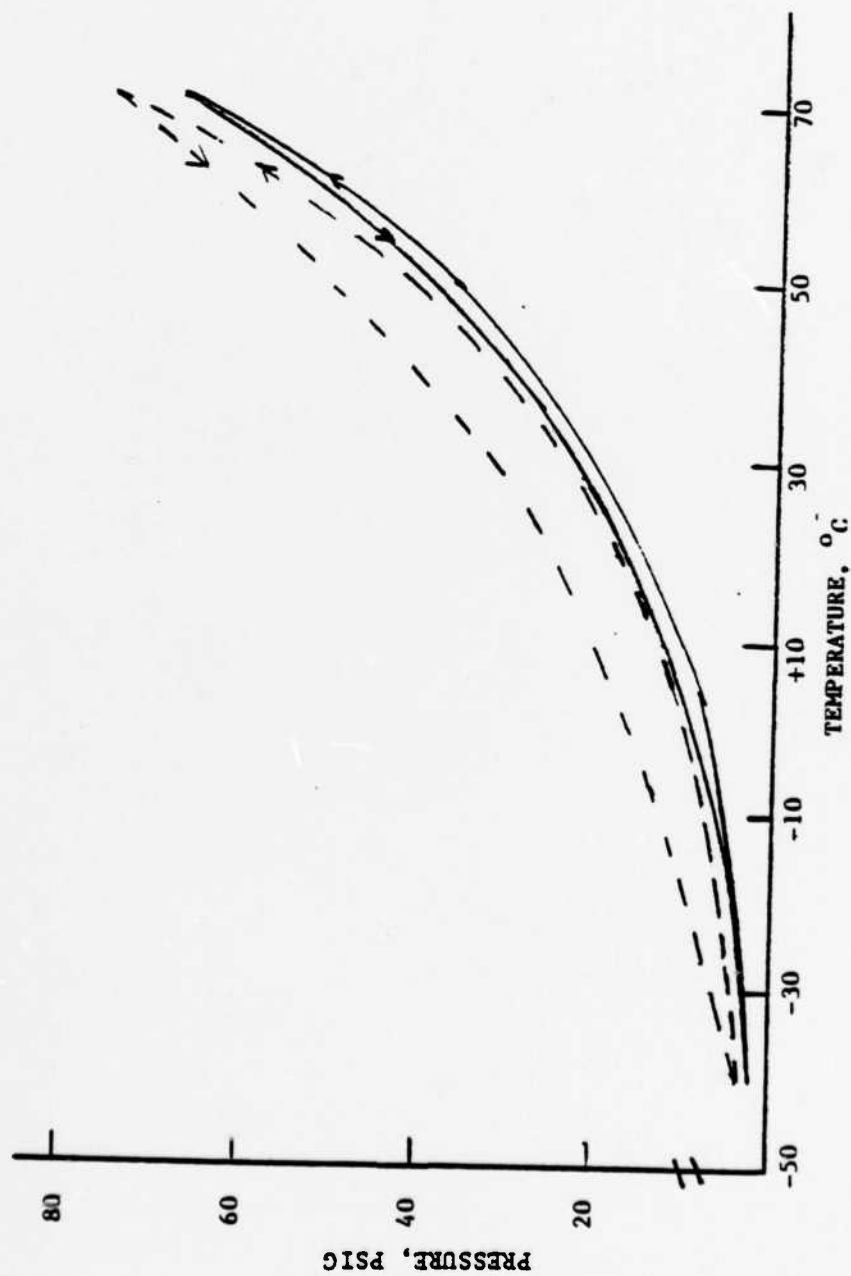


FIGURE 11. HEAT-COOL CYCLES OF  $\text{Li}/\text{SOCl}_2$  D-CELL WITH  $(\text{CoPc})_n$  CATALYZED CATHODE AND  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE AT A CONSTANT CURRENT (CONTINUOUS) DISCHARGE OF  $1 \text{ mA}/\text{cm}^2$ . FIRST CYCLE ----, SIXTH CYCLE - - - - -.

### 3.0 LONG TERM RESERVOIR STORAGE CAPABILITY

Stainless steels in the 300 series are commonly used in Li/SOCl<sub>2</sub> batteries for hardware parts. The popular acceptance of 316L stainless steel is mostly based on its apparent compatibility with LiAlCl<sub>4</sub>·SOCl<sub>2</sub> electrolyte in active primary cells, but no systematic evaluation of its long term storage compatibility with electrolyte for reserve batteries, which require several years of storage, has been carried out.

In this program, the compatibility of both 316L and 321 stainless steel in neutral and acidic electrolytes was evaluated. Stability of the polymeric cobalt phthalocyanine catalyst and its corrosivity effect on 316L and 321 S.S. were also examined in a neutral electrolyte environment.

Glass ampuls were selected to store the electrolyte according to the storage test plan shown in Table 1 and 2. The electrolytes were 1.5M LiAlCl<sub>4</sub>·SOCl<sub>2</sub> and (0.5M LiAlCl<sub>4</sub> + 2.3M AlCl<sub>3</sub>)SOCl<sub>2</sub>. (Acidic electrolyte was included because of the potential application by the Navy for higher rate reserve batteries).

Table 1. Test Plan and Ampul Preparation

Group A	1.5M LiAlCl <sub>4</sub> /SOCl <sub>2</sub> and (CoPc) <sub>n</sub> catalyst
Group B	" and 321 stainless steel
Group C	" and 316L stainless steel
Group D	2.3M AlCl <sub>3</sub> + 0.5M LiAlCl <sub>4</sub> /SOCl <sub>2</sub> and 321 stainless steel
Group E	" " and 316L stainless steel
Group F	1.5M LiAlCl <sub>4</sub> /SOCl <sub>2</sub> and 321 stainless steel and (CoPc) <sub>n</sub> catalyst
Group G	" and 316L stainless steel & (CoPc) <sub>n</sub> catalyst

The sealed ampuls with catalyst (Group F & G) and without catalyst (Group B, C, D and E) were stored at 32°C and 71°C, respectively. Group A ampuls were stored at ambient temperature. In reserve battery applications for the Navy, the maximum operating temperature is 32°C. Since the catalyst is a part of the cathode

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Table 2. Evaluation of Stainless Steel Specimen Compatibility in 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> and (2.3M AlCl<sub>3</sub> + 0.5M LiAlCl<sub>4</sub>)/SOCl<sub>2</sub> Electrolytes

Catalyst	Storage Period (Months)											
	Neutral Electrolyte			Neutral Electrolyte + 321 S.S.						Neutral Electrolyte + 316L S.S.		
	1	4	7	12	1	4	7	12	1	4	7	12
Without	(-)	(-)	(-)	(-)	4 (*)	4 (*)	4 (*)	4	4 (*)	4 (*)	4 (*)	4
					(71°C)	(71°C)	(71°C)	(71°C)	(71°C)	(71°C)	(71°C)	(71°C)
With	4	4	4	4	4	4	4	4	4	4	4	4
					(32°C)	(32°C)	(32°C)	(32°C)	(32°C)	(32°C)	(32°C)	(32°C)

#### Notes

- Stainless steel specimens were stored in sealed glass ampuls.
- Baseline analyses (Time = 0) were conducted on stainless steel samples, electrolyte, and electrolyte + (CoPc)<sub>n</sub>.
- (\*) Repeated for (0.5M LiAlCl<sub>4</sub> + 2.3M AlCl<sub>3</sub>)·SOCl<sub>2</sub> acidic electrolyte.
- (-) These data base are available under a sponsored contract (ARRADCOM).

composition and thus physically separated from the electrolyte during storage, the catalyst experiences operating temperature conditions only at 32°C (max).

The thionyl chloride from Moday Chemicals was distilled once before electrolyte preparation. The 1.5M  $\text{LiAlCl}_4 \cdot \text{SOCl}_2$  solution was made by adding 1.5 moles of dried LiCl (Fisher Chemicals) and 1.5M  $\text{AlCl}_3$  (Fluka Grade) to the distilled  $\text{SOCl}_2$  in a 1 liter flask. The acidic electrolyte was made by adding 0.5 mole of LiCl and 2.8 moles of  $\text{AlCl}_3$ . Both electrolytes were mechanically stirred for 1-2 hours. Each ampul contained 10 ml of electrolyte.

The 316L and 321 stainless steels tested in these studies were sheared into strips 0.2" wide and 2" long. The 316L stainless steel was 0.005" thick; the 321 stainless steel was 0.025". Only half of the length of these specimens was immersed in the electrolyte and the other half remained above the electrolyte in a sealed ampul.

In preparation for storage, the stainless steel strips were washed in a hot (70°C) solution of 170 g Pennwalt Alkaline Detergent #36 cleaner in 1500 ml  $\text{H}_2\text{O}$ , heated in this solution for 5 minutes, and then rinsed with water. After rinsing, they were placed for 10 minutes in a 45°C pickling solution containing 20% by weight of water, followed by another rinsing in two successive  $\text{H}_2\text{O}$  baths. After the double rinsing, the strips were placed for 30 minutes in a hot (55°C) passivation solution made by slowly adding first 500 ml of conc.  $\text{HNO}_3$  and then 56.2 g  $\text{Na}_2\text{Cr}_2\text{O}_7$  to 2 liters of water, after which they were washed again in two successive  $\text{H}_2\text{O}$  baths. The strips were then dried of their excess water with paper towels and vacuum dried at 110°C overnight.

The  $(\text{CoPc})_n$  catalyst was synthesized and washed with 5% HCl to remove uncomplexed cobalt ions. It was then heat treated at 550°C for two hours in an inert atmosphere. After cooling to ambient temperature, 0.11 g was added to each storage ampul.

#### EVALUATION OF ELECTROLYTE AND STAINLESS STEEL SPECIMENS

Four ampuls from each group were taken out of storage for cobalt and iron analysis after each period. The ampuls containing stainless steel, both with and without



catalyst, had undergone some yellow discoloration, more intense with the acidic electrolytes than with neutral electrolytes. The intensity of discoloration increased with storage time. After breaking the ampuls, the electrolyte was vacuum filtered, and 12 ml of distilled water was added to decompose  $\text{SOCl}_2$ .

• Electrolyte

To determine the presence of cobalt, a few drops of 1, 10-phenanthroline in 50:50 methanol-water (1% by weight) was added to the aqueous solution. A light blue color would indicate the presence of cobalt ions, but none of the ampuls tested so indicated - showing the catalyst to be stable for 12-month storage.

Quantitative determination of Fe was done (using U.V. absorption technique) on all groups of ampuls by pipetting 5 ml of electrolyte solution into a 100 ml flask, adding 15-20 ml of water, and allowing the mixture to cool. The following reagents, in the order listed, were added:

- a) 30 ml of a 50:50 (by volume) mixture of methyl ethyl ketone and methanol
- b) 5 ml of a 30% by weight  $\text{NH}_4\text{SCN}$  solution
- c) 5 ml of a 10% by weight  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution
- d) 10 ml of 1:1  $\text{HCl}$  solution
- e) Dilute to mark with deionized water and mix well

A blank containing all reagents, except the electrolyte solution, was also made.

The presence of iron in these solutions gave an orange coloring. The absorbance of each versus the blank was measured at 475 nm using the Bausch and Lomb Spectronic 20. The concentrations in each solution are given in Table 3, as based on a single absorption experiment.

Table 3. Iron Concentration in the Electrolyte After Storage

Group	Fe Concentration, $\mu\text{g/ml}$ of Electrolyte			
	<u>1 Month</u>	<u>4 Months</u>	<u>7 Months</u>	<u>12 Months</u>
A	8.65	8.70	21.65	9.93
B	3.02	4.56	2.65	2.84
C	2.65	3.08	2.84	3.15
D	3.80	4.69	13.32	8.08
E	2.22	3.08	5.42	5.30
F	14.25	13.01	20.10	21.03
G	7.90	12.00	21.03	17.0
1.5M $\text{LiAlCl}_4/\text{SOCl}_2$	1.60	-	-	-
(2.3M $\text{AlCl}_3$ + 0.5M $\text{LiAlCl}_4$ )/ $\text{SOCl}_2$	0.37	-	-	-

Examination of Table 3 reveals that the iron concentration in the electrolyte in Groups B to E remains unchanged whereas in Groups F and G it increases slightly. The source of iron in ampul A was identified to be the stainless steel container used to heat treat the  $(\text{CoPc})_n$  catalyst at  $550^\circ\text{C}$ . Therefore, the higher values found in Groups F and G are the sum of the contamination in Groups A and B, and A and C, respectively. Since the stainless steel specimen did not contribute Fe contamination on storage in thionyl chloride electrolyte, experiments were not repeated with a Fe free  $(\text{CoPc})_n$  catalyst.

• Stainless Steel Specimens

The stainless steel specimens were separated from the electrolyte after reaching their storage periods noted in Table 2. The samples were washed with pure  $\text{SOCl}_2$  and the excess solvent was removed with soft paper towels and dried under vacuum for several days (at least 7 days).

The specimens immersed in the neutral electrolyte showed no visible signs of corrosion, however, both the 316L and 321 strips stored in the acidic electrolyte showed light brown discoloration of their surface that were not immersed in the electrolyte. The surface and microstructural integrity of the electrolyte immersed and non-immersed portions of all stored specimens were subjected to both SEM and metallographic analysis.

SEM photomicrographs of stainless steel surfaces, fresh and after 4- and 12-month storage at  $71^\circ\text{C}$ , are shown in Figures 12-32. The photomicrographs show that 316L and 321 stainless steel surfaces were corroded in both the neutral and acidic electrolytes. The acidic electrolyte attacked the surface much more severely than neutral electrolyte. The surface corrosion appeared to slow down with storage time by the corrosion film. The part of the specimen that was not immersed, but exposed to electrolyte vapor, also exhibited surface corrosion similar to the part immersed directly in the electrolyte.

In order to evaluate the depth of the corrosion film, the cross sections of the specimens were examined by optical metallographis technique.

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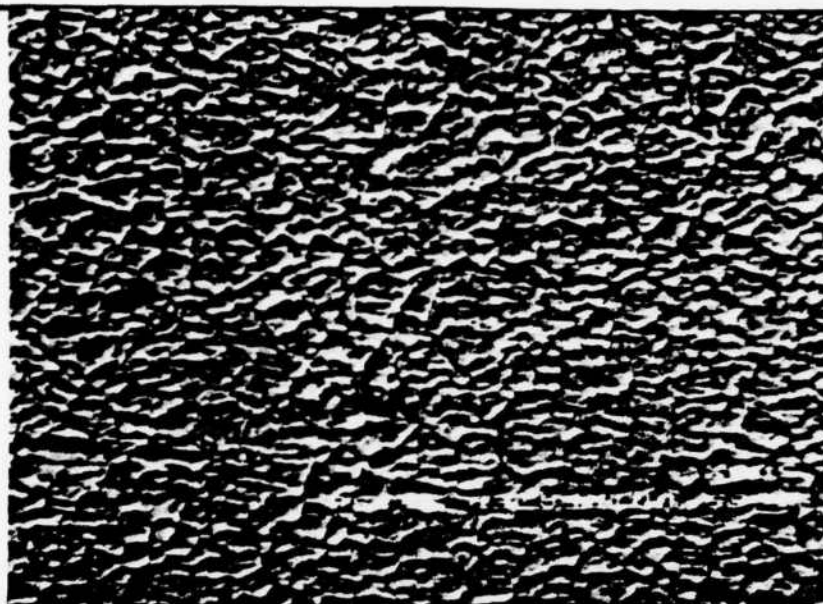
Li/SOCl<sub>2</sub> Safety Studies



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200X



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FIGURE	METALLURGICAL LABORATORY LOG NUMBER	COGNIZANCE
12	6669	J. Kasell - N Doddapaneni

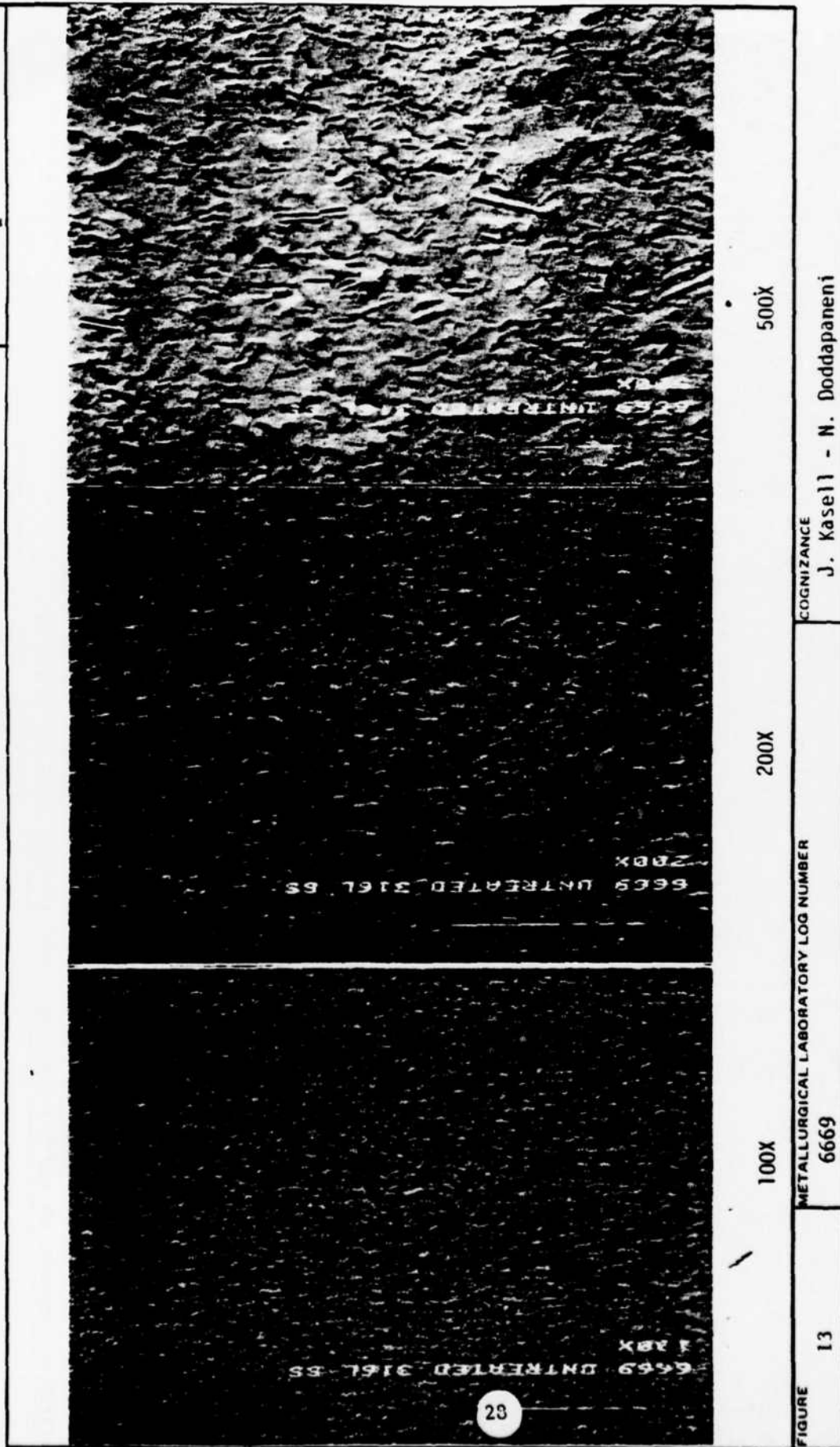
Electron micrographs of the 321 stainless steel without exposure to Li/SOCl<sub>2</sub>.

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Electron micrographs of the 316L stainless steel without exposure to Li/SOCl<sub>2</sub>.

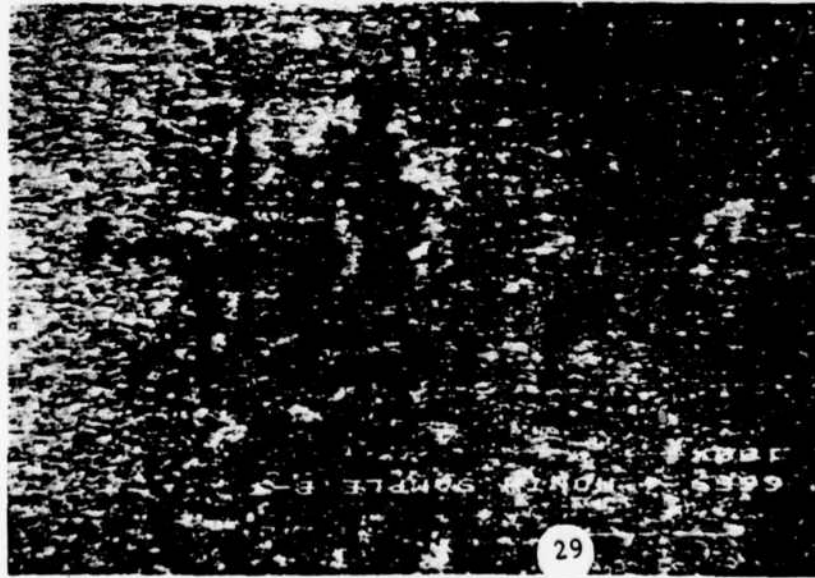


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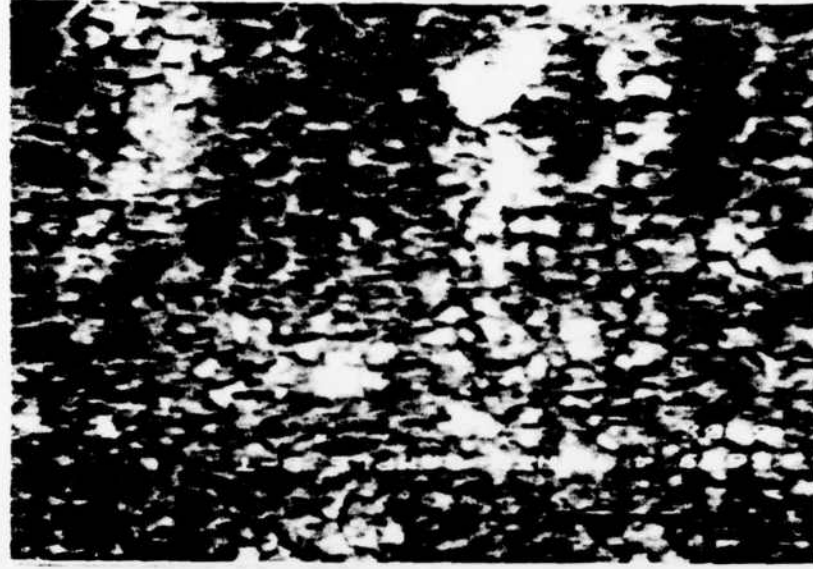
Li/SOCl<sub>2</sub> Safety Studies



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FIGURE

14

METALLURGICAL LABORATORY LOG NUMBER

6669

COGNIZANCE

J. Kasell - N. Doddapaneni

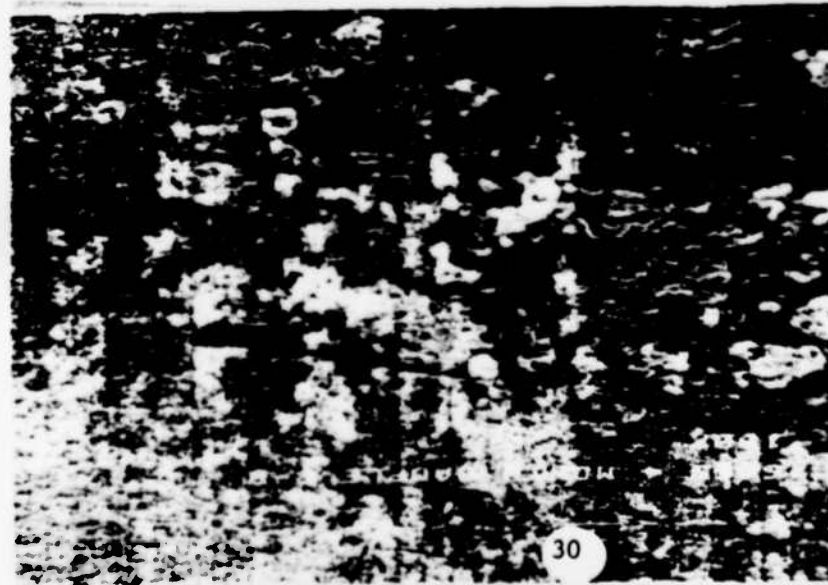
Electron micrographs of sample B Top after a four month exposure to Li/SOCl<sub>2</sub>.

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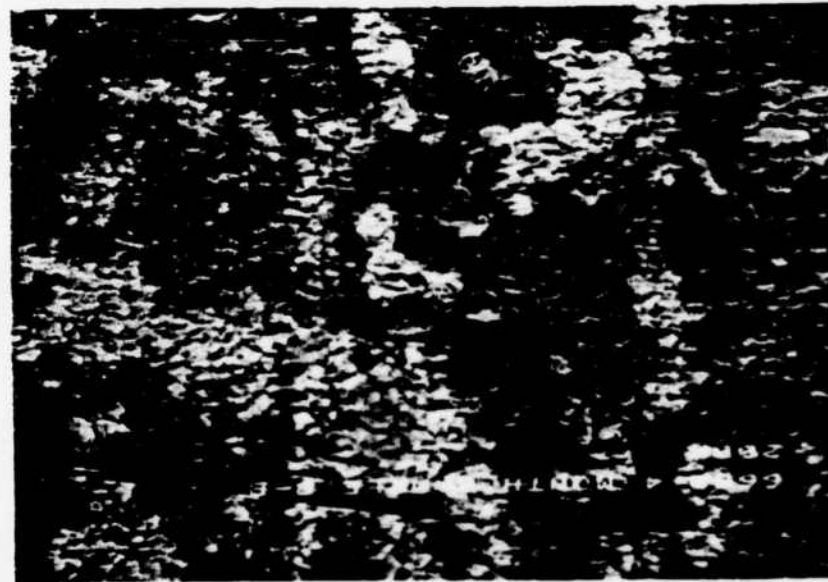
Honeywell

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



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FIGURE

15

METALLURGICAL LABORATORY LOG NUMBER

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COGNIZANCE

J. Kasell - N. Doddapeneni

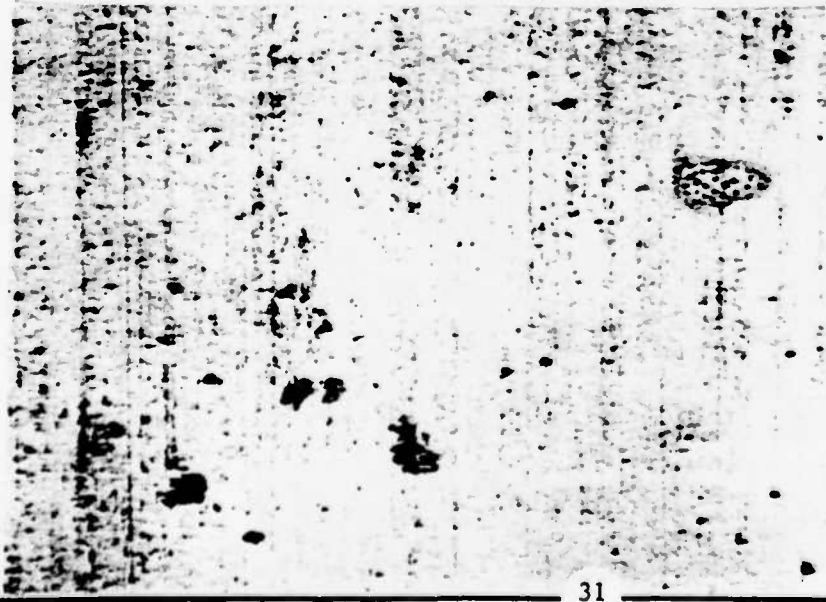
Electron micrographs of sample B bottom after a four month exposure to Li/SOCl<sub>2</sub>.

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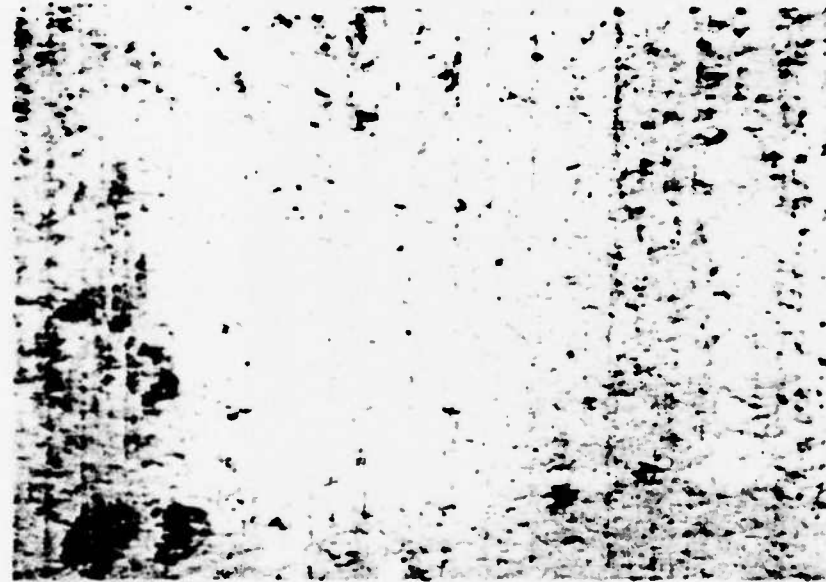
# Honeywell

DEVICE/PART NUMBER

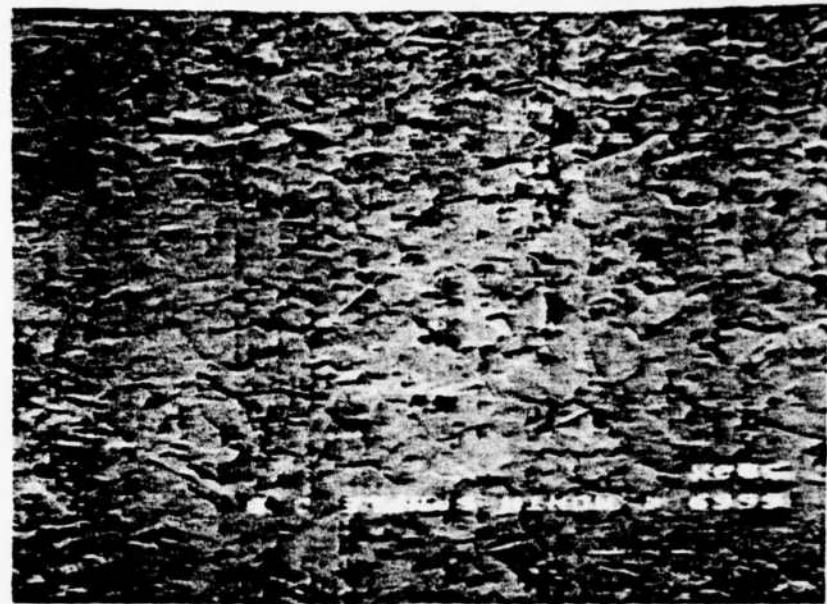
Li/SOCl<sub>2</sub> Safety Studies



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FIGURE

16

METALLURGICAL LABORATORY LOG NUMBER

6669

COGNIZANCE

J. Kasell - N. Doddapaneni

Electron micrographs of sample C bottom after four months exposure to Li/SOCl<sub>2</sub>.

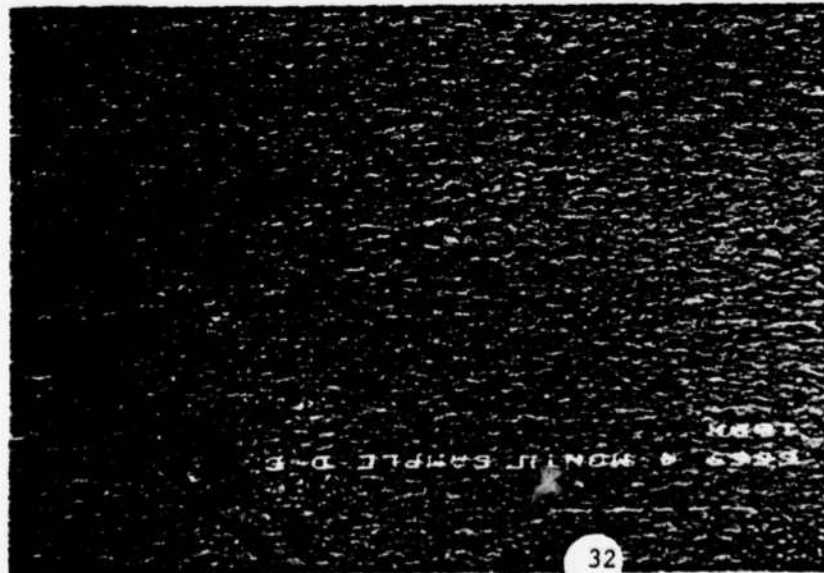


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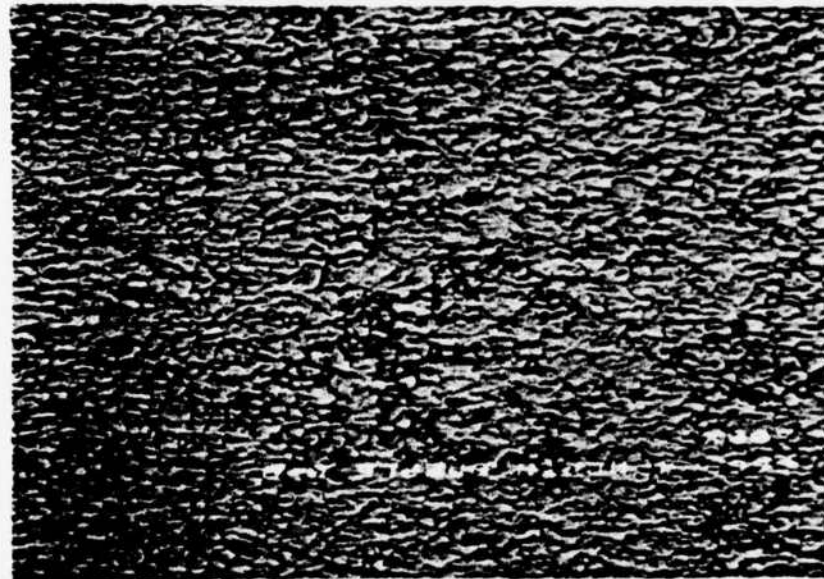
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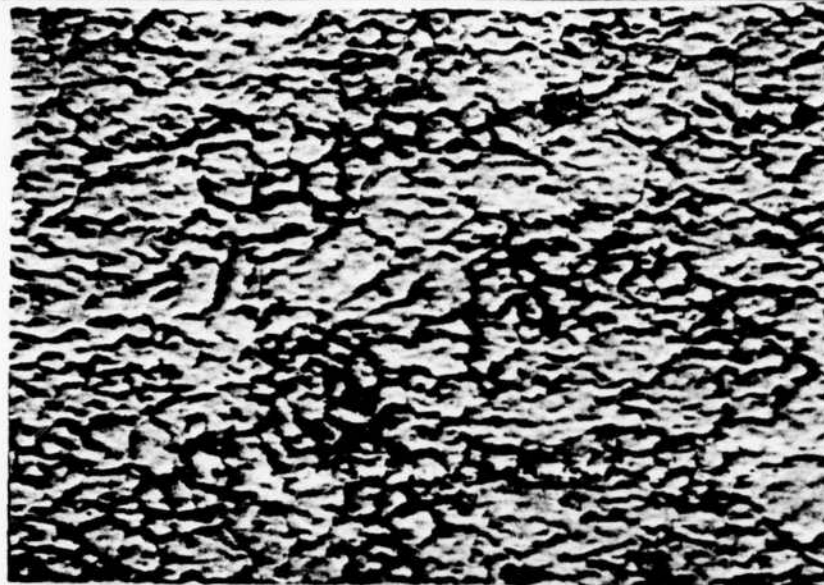
Li/SOCl<sub>2</sub> Safety Studies



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FIGURE

17

METALLURGICAL LABORATORY LOG NUMBER

6669

COGNIZANCE

J. Kasell - N. Doddapaneni

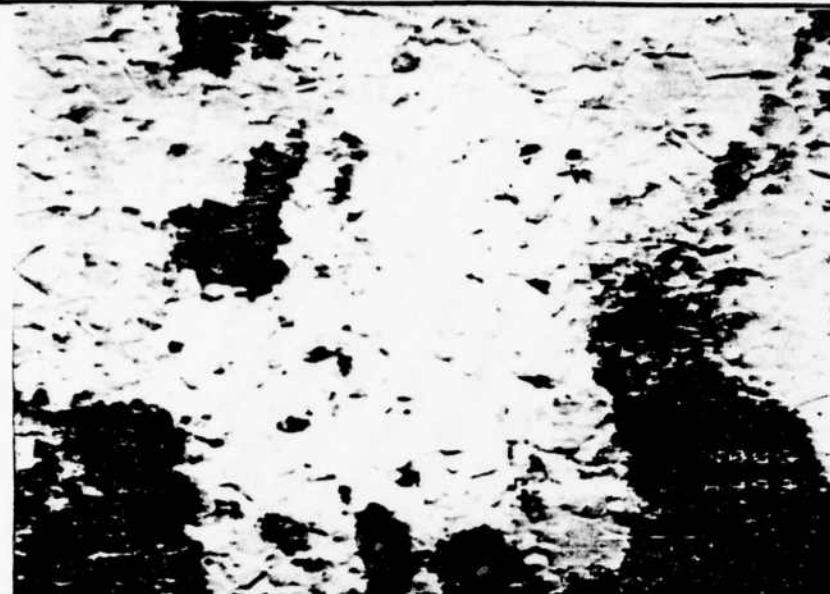
Electron micrographs of sample D bottom after four months exposure to Li/SOCl<sub>2</sub>.

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Li/SOCl<sub>2</sub> Safety Studies



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FIGURE

18

M&PE LOG NUMBER

6669

COGNIZANCE

J. Kasell - N. Doddapaneni

FTR NUMBER

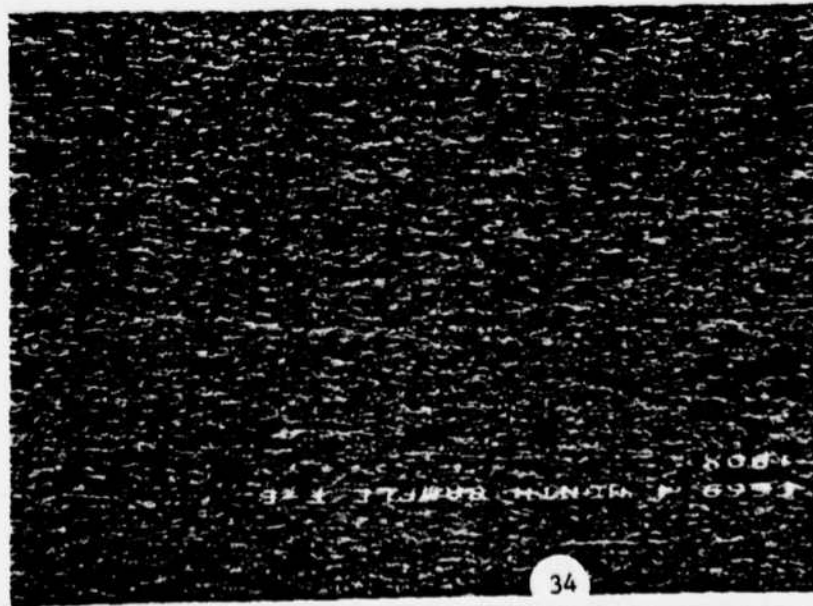
Electron micrographs of sample E bottom after a four month exposure to Li/SOCl<sub>2</sub>.

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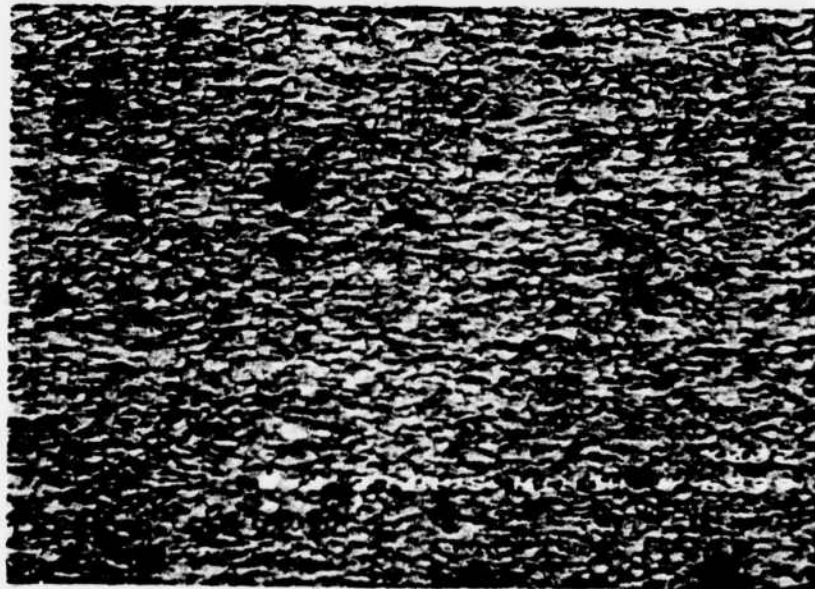
**Honeywell**

DEVICE/PART NUMBER

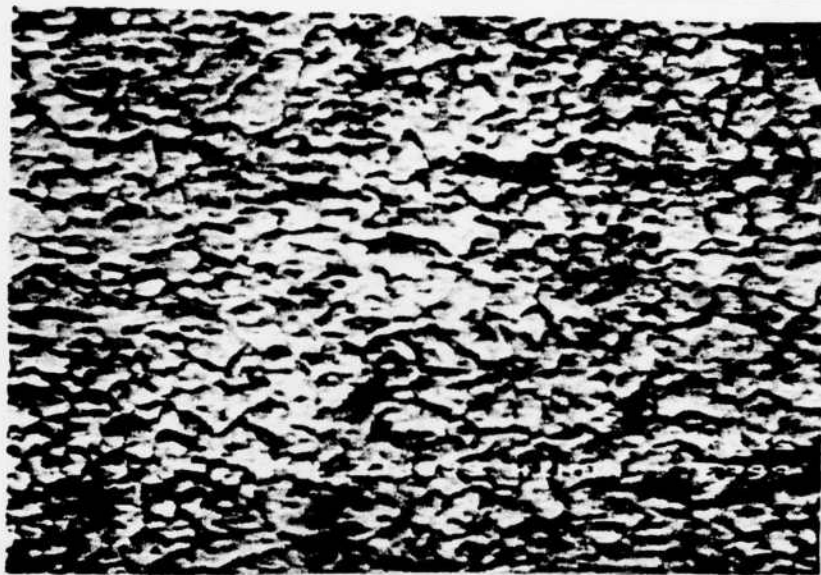
Li/SOCl<sub>2</sub> Safety Studies



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FIGURE	M&PE LOG NUMBER	COGNIZANCE	ETH NUMBER
19	6669	J. Kasell - N. Doddapaneni	

Electron micrographs of sample F bottom after four months exposure to Li/SOCl<sub>2</sub>.

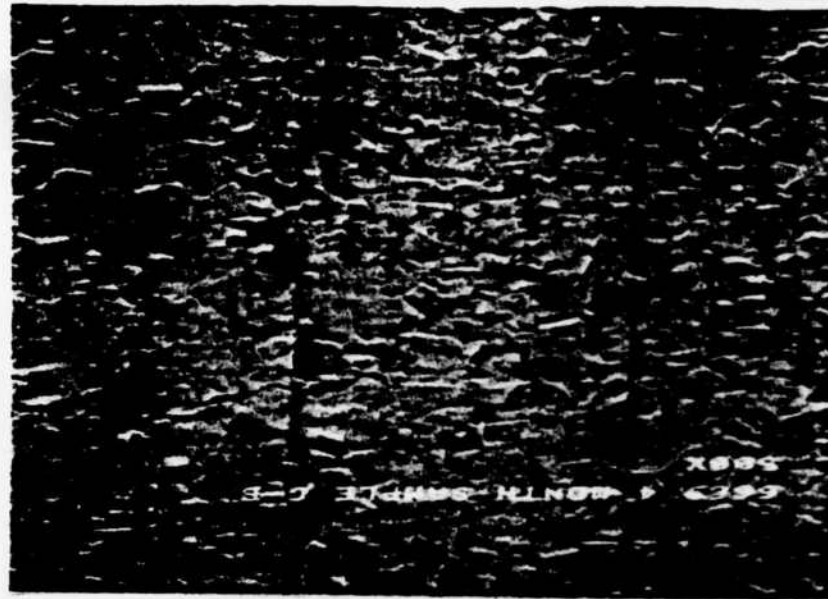
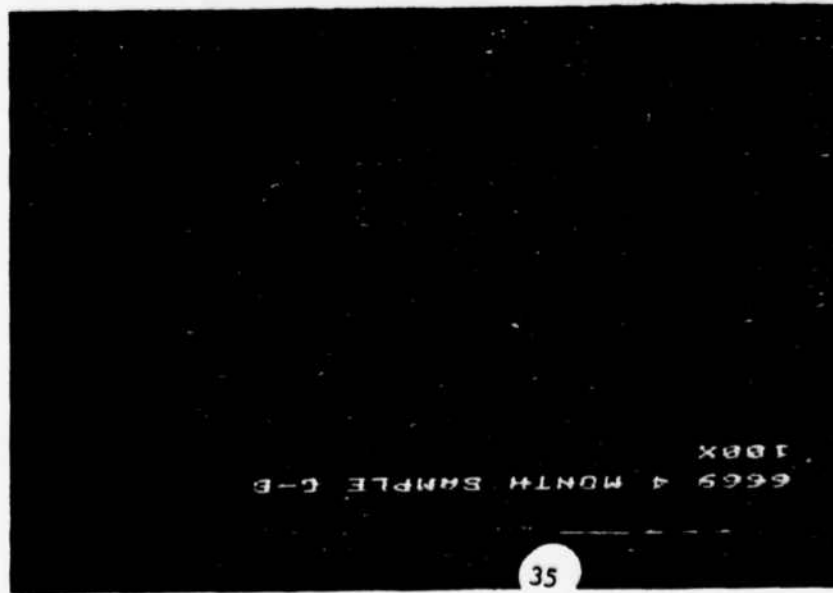


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HOPKINS, MN 55343

**Honeywell**

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



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200X

500X

FIGURE	20	MAPE LOG NUMBER	6669	COGNIZANCE	J. Kasell - N. Doddapaneni	FTR NUMBER
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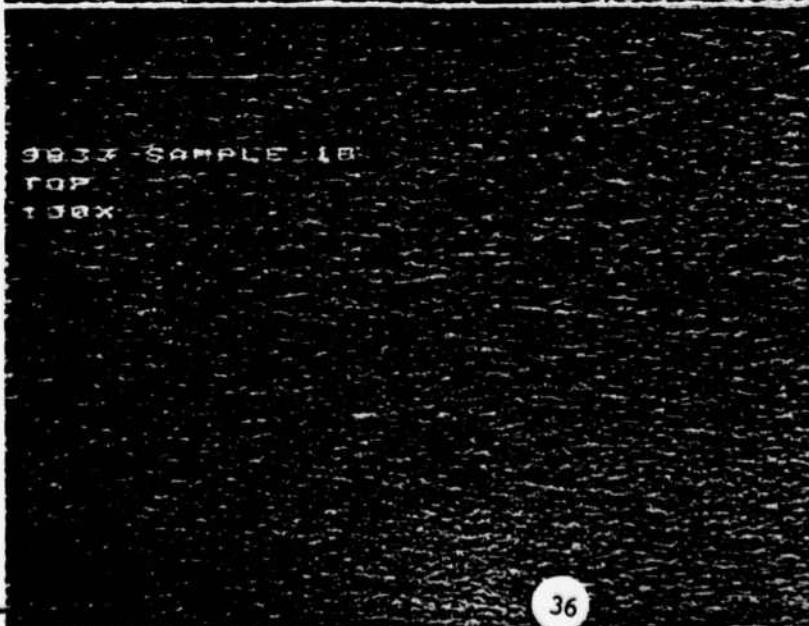
Electron micrographs of sample G bottom after four months exposure to Li/SOCl<sub>2</sub>.

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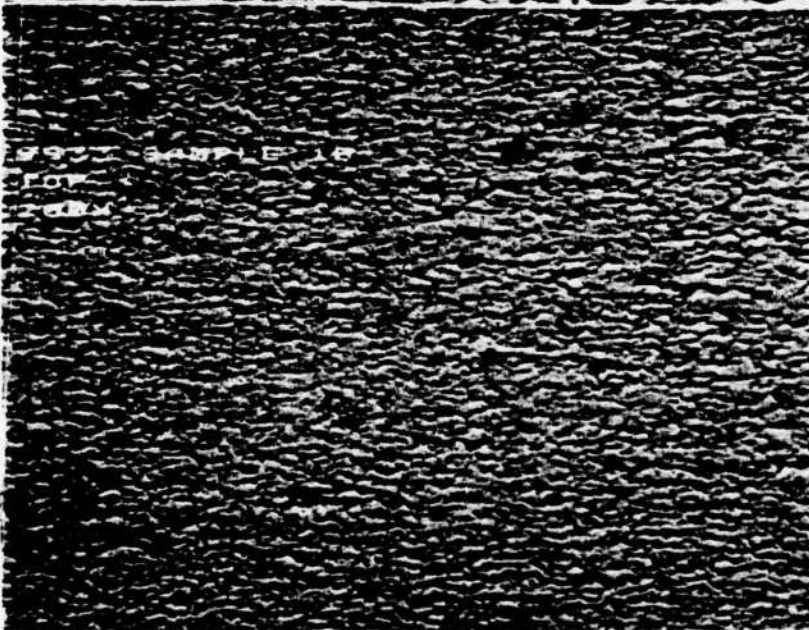
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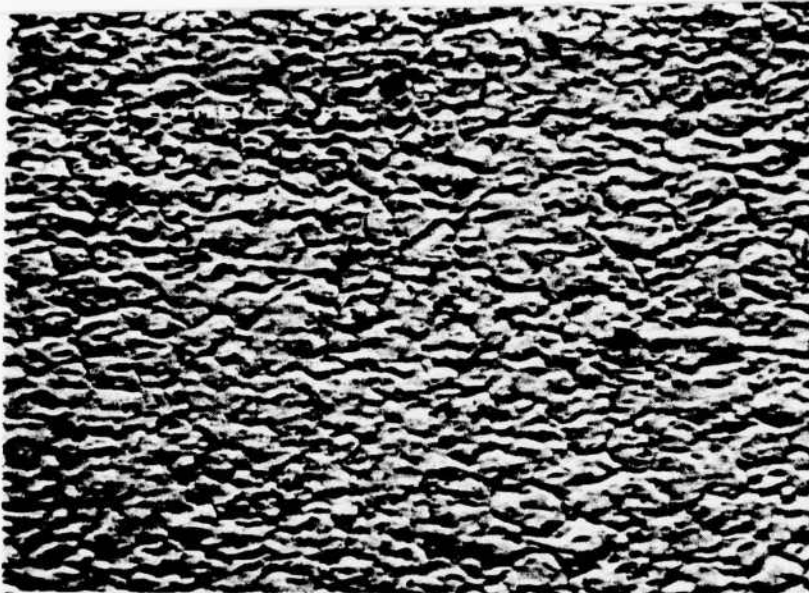
Li/SOCl<sub>2</sub> Safety Studies



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FIGURE 21

9833

B. Schrupp/N. Doddapaneni

FIGURE NUMBER

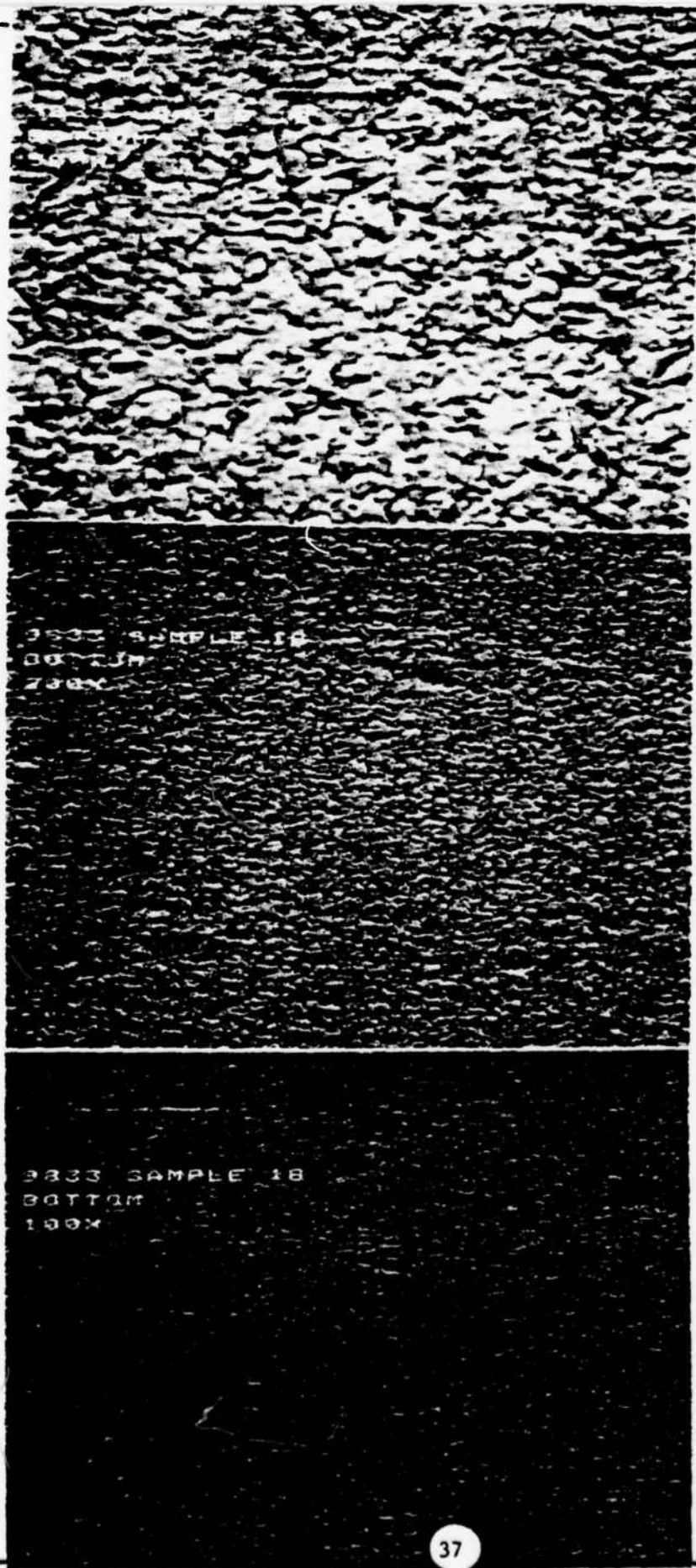
Electron micrographs of sample 1B (top) after twelve months exposure to Li/SOCl<sub>2</sub>

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600 SECOND STREET NE  
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# Honeywell

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



100X

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FIGURE 22

9833

B. Schrupp, N. (oddly named)

FILE NUMBER 11

Electron micrographs of sample 1B (bottom) after twelve months exposure to Li/SOCl<sub>2</sub>.

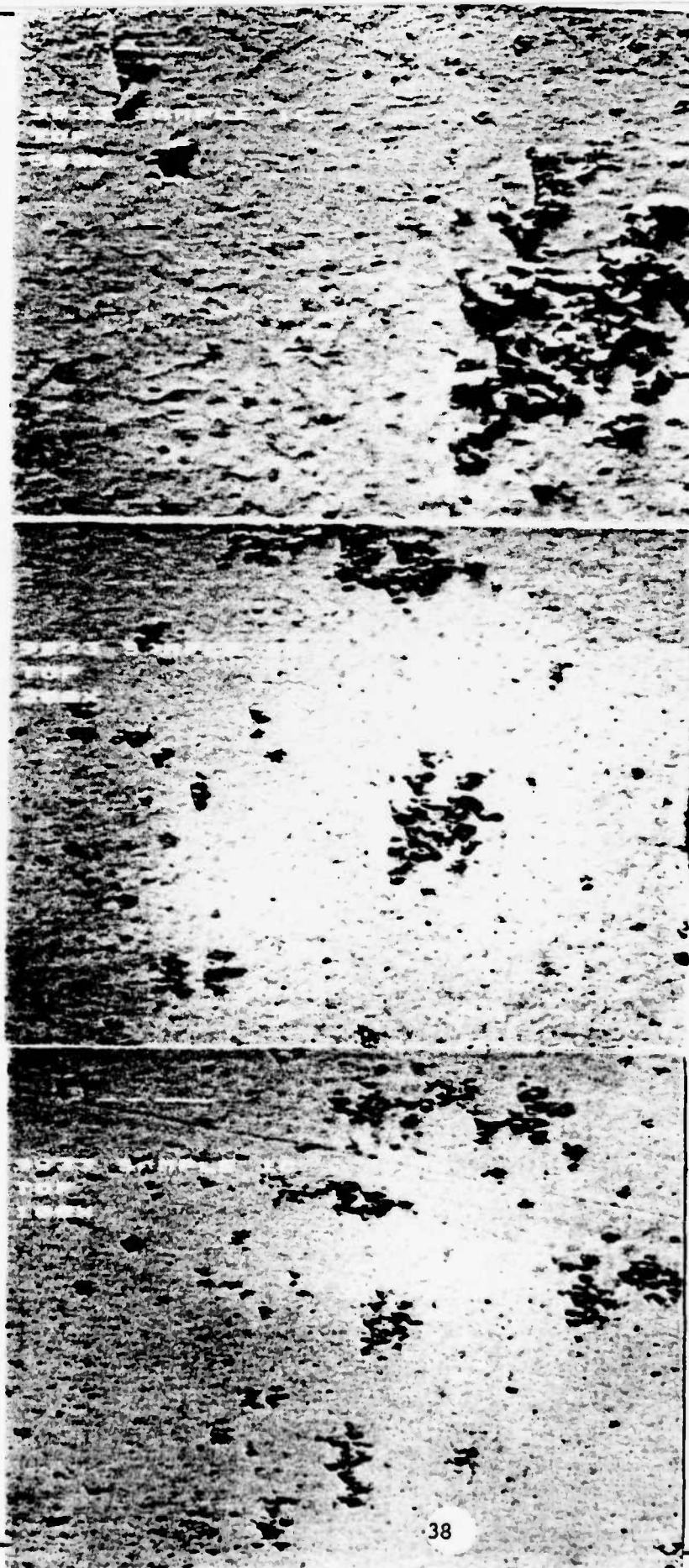


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DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



38

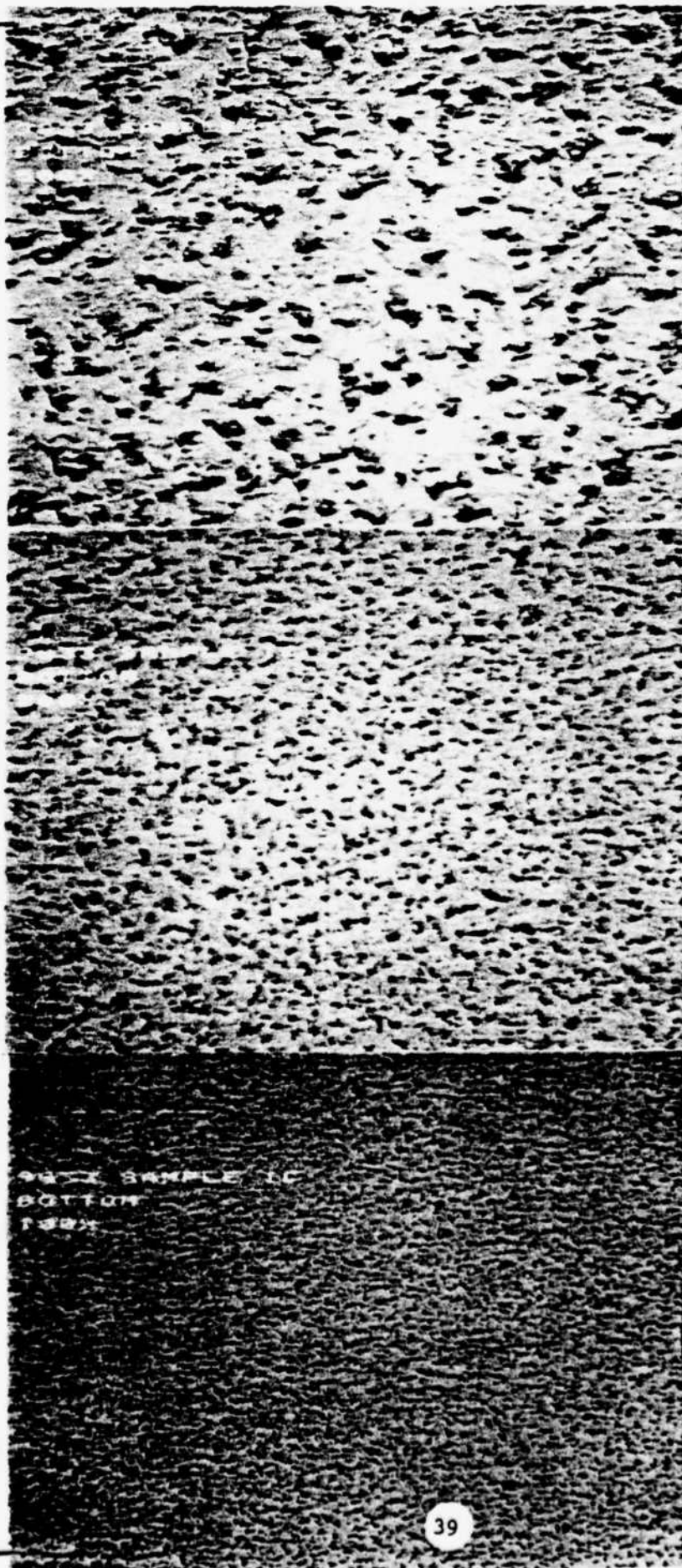
100X		200X		500X	
FIGURE	23	MAPE LOG NUMBER	9833	COGNIZANCE	B. Schrupp/N. Doddapaneni
				FIGURE NUMBER	

Electron micrographs of sample 1C (top) after twelve months exposure to Li/SOCl<sub>2</sub>.

DEFENSE SYSTEMS DIVISION  
800 SECOND STREET NE  
HOPKINS, MN 55343

**Honeywell**

DEVICE/PART NUMBER  
Li/SOCl<sub>2</sub> Safety Studies



100X

200X

500X

FIGURE	24	MEPE LOG NUMBER	9833	COGNIZANCE	B. Schrupp/N. Doddapaneni	FTR NUMBER
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Electron micrographs of sample 1C (bottom) after twelve months exposure to Li/SOCl<sub>2</sub>.

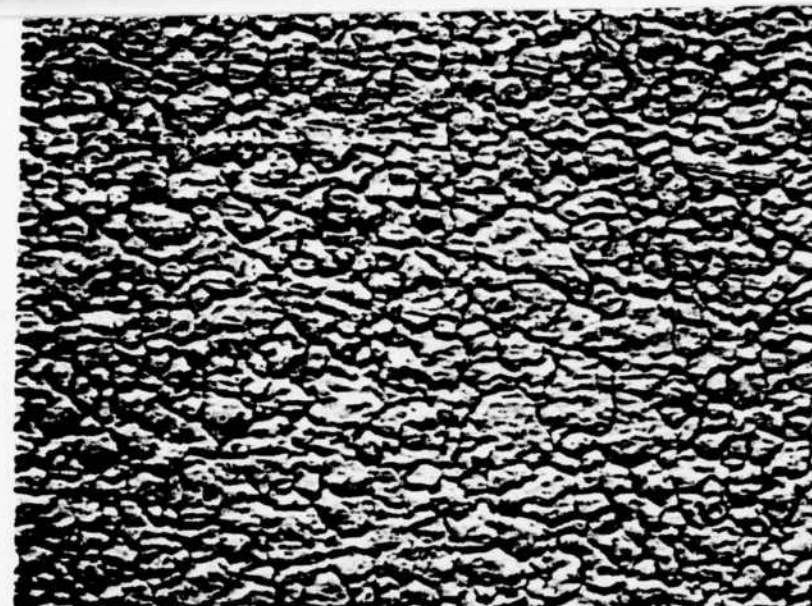
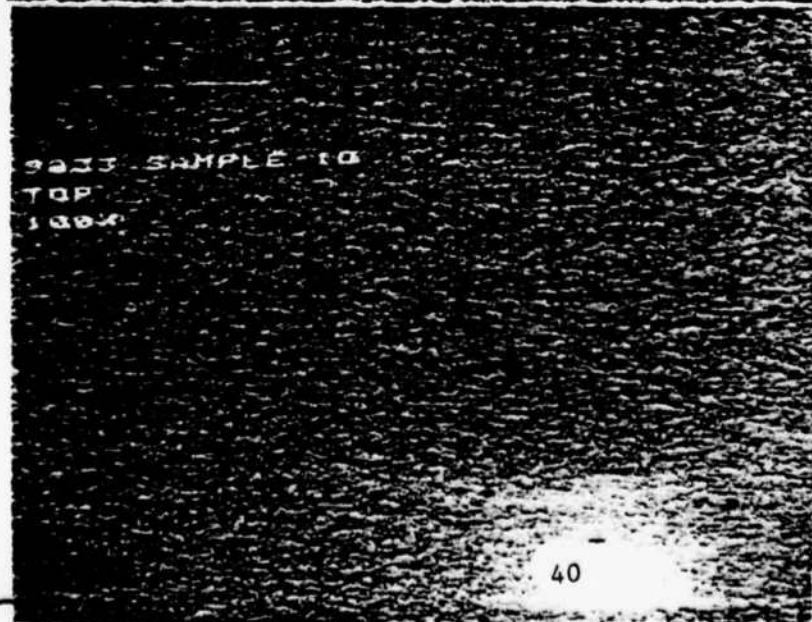


DEFENSE SYSTEMS DIVISION  
600 SECOND STREET NE  
HOPKINS, MN 55343

**Honeywell**

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



100X

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FIGURE

25

MEMO FILE NUMBER

9833

B. Schrupp/N. Boddapant

FILE NUMBER

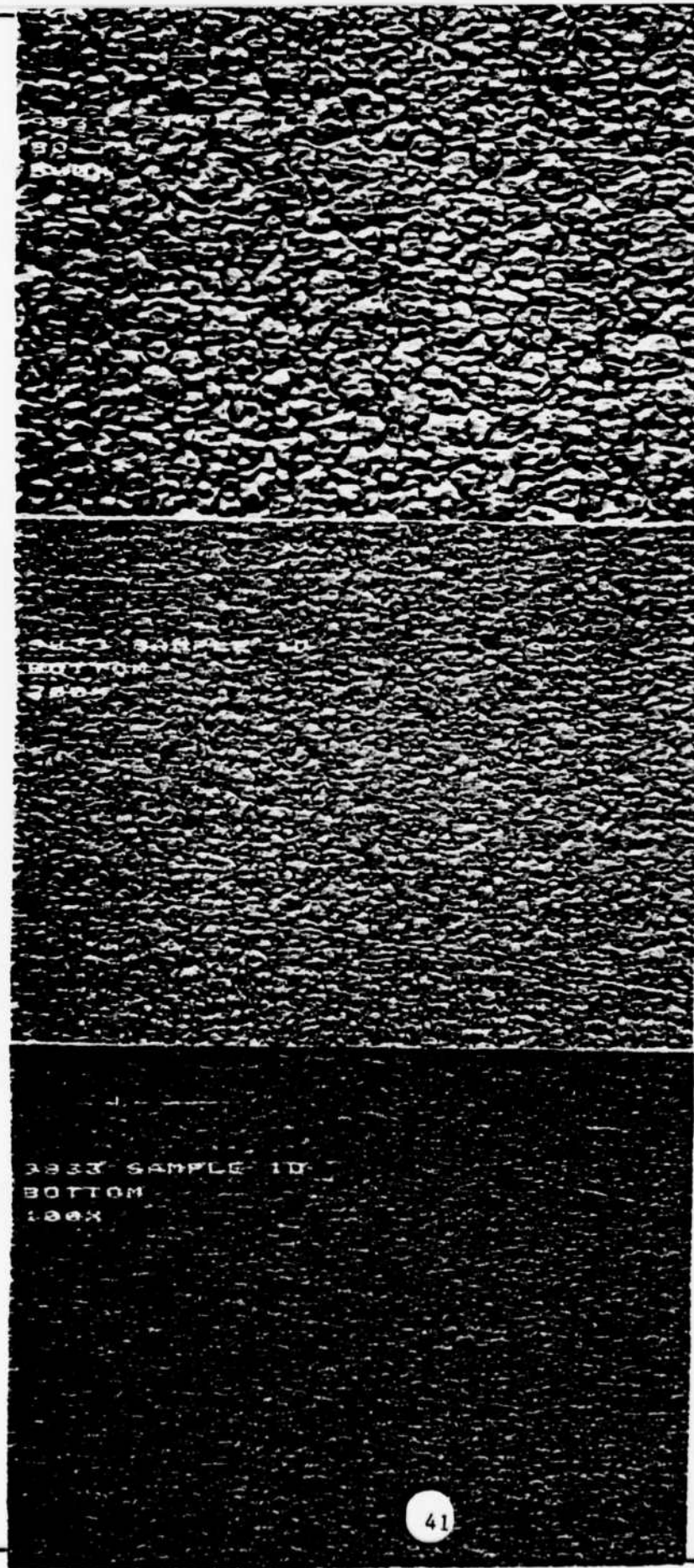
Electron micrographs of sample 1D (top) after twelve months exposure to Li/SOCl<sub>2</sub>.

DEFENSE SYSTEMS DIVISION  
600 SECOND STREET NE  
HOPKINS, MN 55343

**Honeywell**

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



41

100X

200X

500X

FIGURE	26	MAPE LOG NUMBER	9833	COGNIZANCE	B. Schrupp/N. Doddapaneni	FILE NUMBER	14
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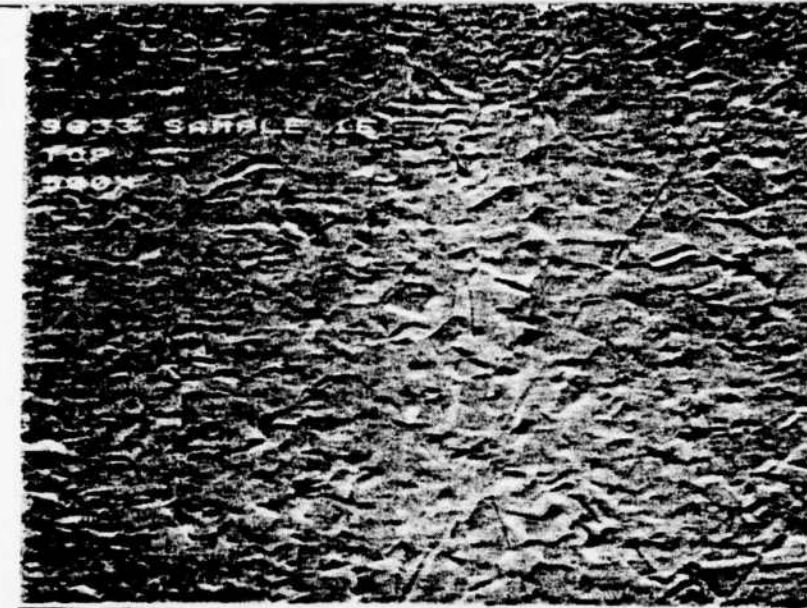
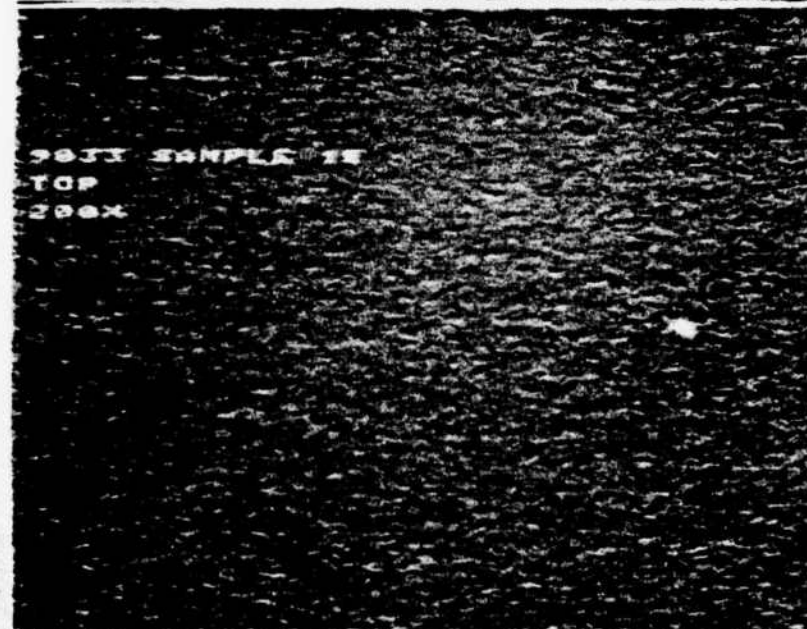
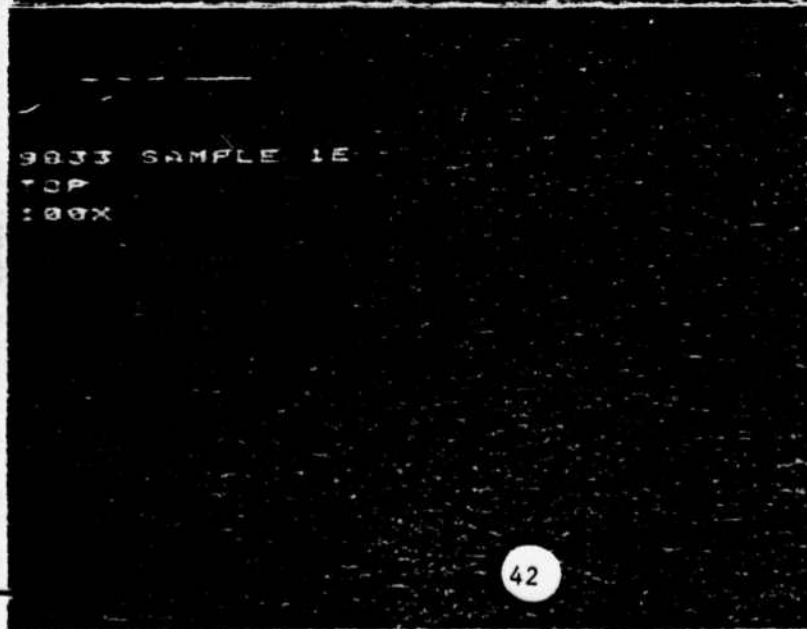
Electron micrographs of sample 1D (bottom) after twelve months exposure to Li/SOCl<sub>2</sub>.

DEFENSE SYSTEMS DIVISION  
600 SECOND STREET NW  
HOPKINS, MN 55343

Honeywell

DEVICE/PART NUMBER

L1/SOCl<sub>2</sub> Safety Studies



42

100X

200X

500X

FIGURE	27	M&PE LOG NUMBER	9833	COGNIZANCE	B. Schrupp/N. Doddapaneni	FTR NUMBER

Electron micrographs of sample 1E (top) after twelve months exposure to L1/SOCl<sub>2</sub>.



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100X

200X

500X

FIGURE  
28

MAPE LOG NUMBER  
9833

COGNIZANCE  
B. Schrupp/N. Doddapaneni

ETH NUMBER

Electron micrographs of sample 1E (bottom) after twelve months exposure to Li/SOCl<sub>2</sub>.

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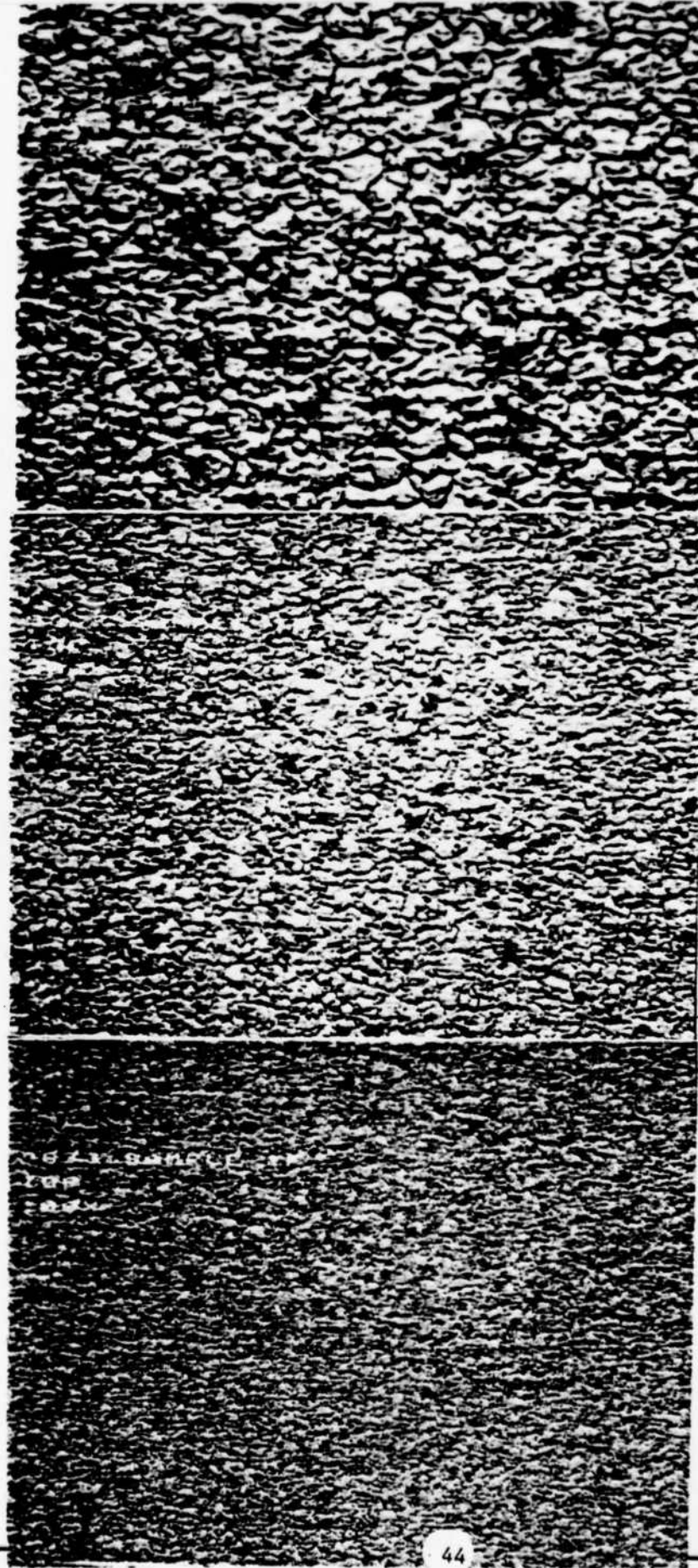


FIGURE  
29

MAPE LOG NUMBER  
9833

COGNIZANCE

B. Schrupp/N. Doddapaneni

FIGURE 11

Electron micrographs of sample 1F (top) after twelve months exposure to Li/SOCl<sub>2</sub>.

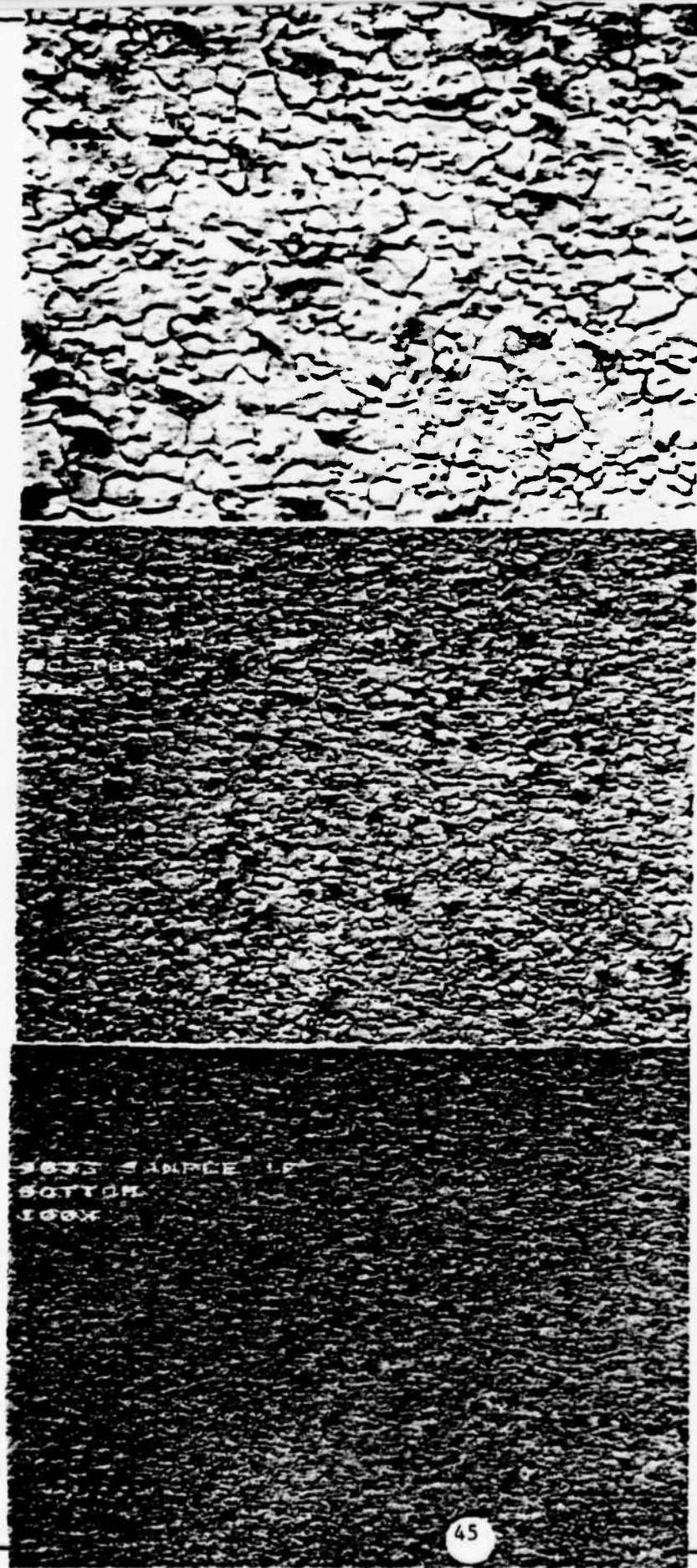


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DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



100X

200X

500X

FIGURE  
30

MSA LOG NUMBER IF  
9833

B. Schrupp/H. Boddapantani

FILE NUMBER IF

Electron micrographs of sample 1F (bottom) after twelve months exposure to Li/SOCl<sub>2</sub>.

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DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Studies



100X

200X

500X

FIGURE

31

MAPE LOG NUMBER

9833

COGNIZANCE

B. Schrupp/N. Doddapaneni

ETH NUMBER

Electron micrographs of sample 1G (top) after twelve months exposure to Li/SOCl<sub>2</sub>.

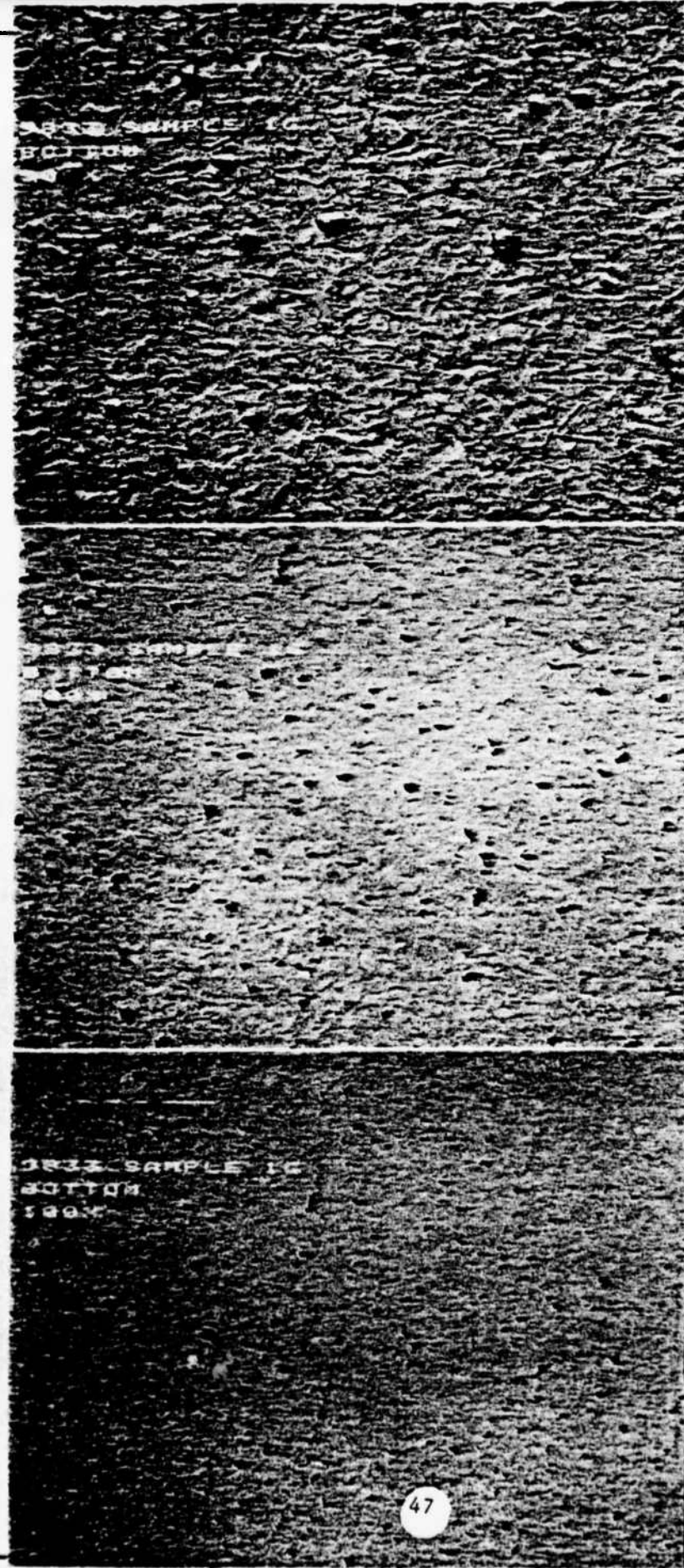


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**Honeywell**

DEVICE/PART NUMBER

L1/SOCl<sub>2</sub> Safety Studies



100X

200X

500X

FIGURE  
32

MS&PE LOG NUMBER  
9833

COGNIZANCE

B. Schrupp/N. Doddapaneni

ETR NUMBER

Electron micrographs of sample 1G (bottom) after twelve months exposure to L1/SOCl<sub>2</sub>.



The specimens were then cut and the edges were polished and etched before they were metallographically examined. Both the immersed and non-immersed (i.e., exposed to vapor phase) edges of the specimens were studied.

In Figure 33, the photomicrographs of the edges of fresh 321 and 316L stainless steel specimens are given. The optical metallographic studies of these specimens after exposure to both acidic and neutral electrolyte for 1, 4 and 7 months (12-month stored specimens were not analyzed by this technique) at 71°C revealed no significant penetration of corrosion into the specimens. For example, the photomicrographs of specimens after 7-month exposure showed no significant difference from specimen-to-specimen (Figures 34 - 39). Based on this limited study, it can be concluded that the surface corrosion of both 316L and 321 stainless steel specimens takes place and that these surface films either eliminate or significantly reduce further corrosion in both acidic and neutral electrolyte. In addition, the presence of  $(\text{CoPc})_n$  catalyst does not appear to affect the surface corrosion.

In conclusion, we believe that both 316L stainless steel and 321 stainless steel can be used as materials of construction for the electrolyte reservoir in reserve batteries. In cell design that uses stainless steel as the positive collector grid, however, the influence of the surface film on cell polarization should be determined, especially in applications that require high intermittent pulses during a long operating mission life.

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A



B

FIGURE

33

METALLURGICAL LABORATORY LOG NUMBER

6669

COGNIZANCE

D. Dehmer - D. Doddapaneni

Photomicrographs of both edges of the untreated 321 stainless steel (View A) and the untreated 316L stainless steel (View B)

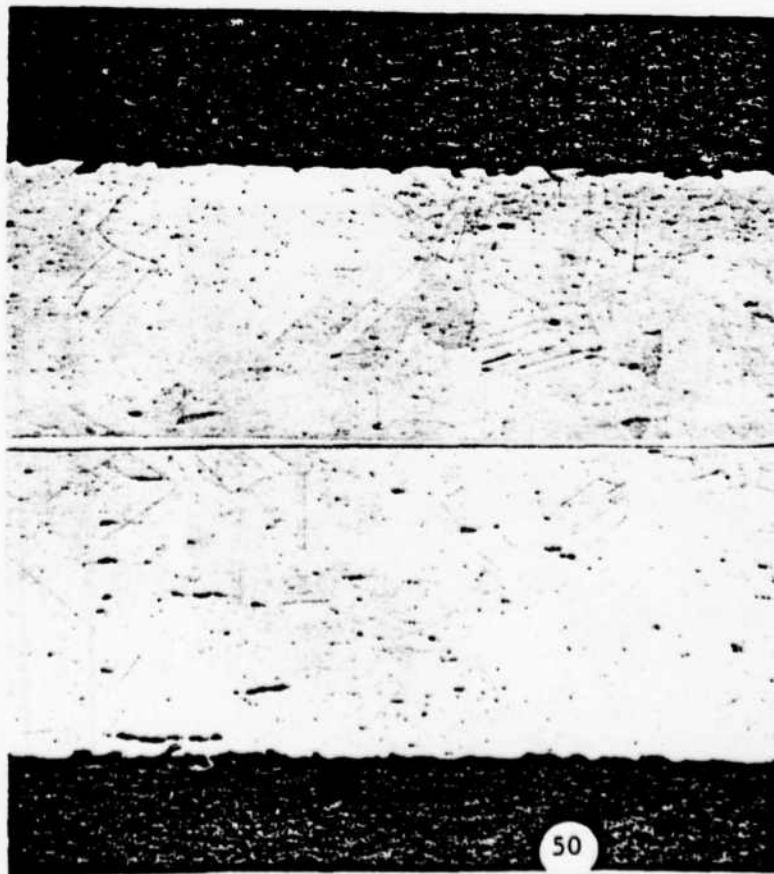
Magnification: 575X.

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600 SECOND STREET NE  
HOPKINS, MN 55343

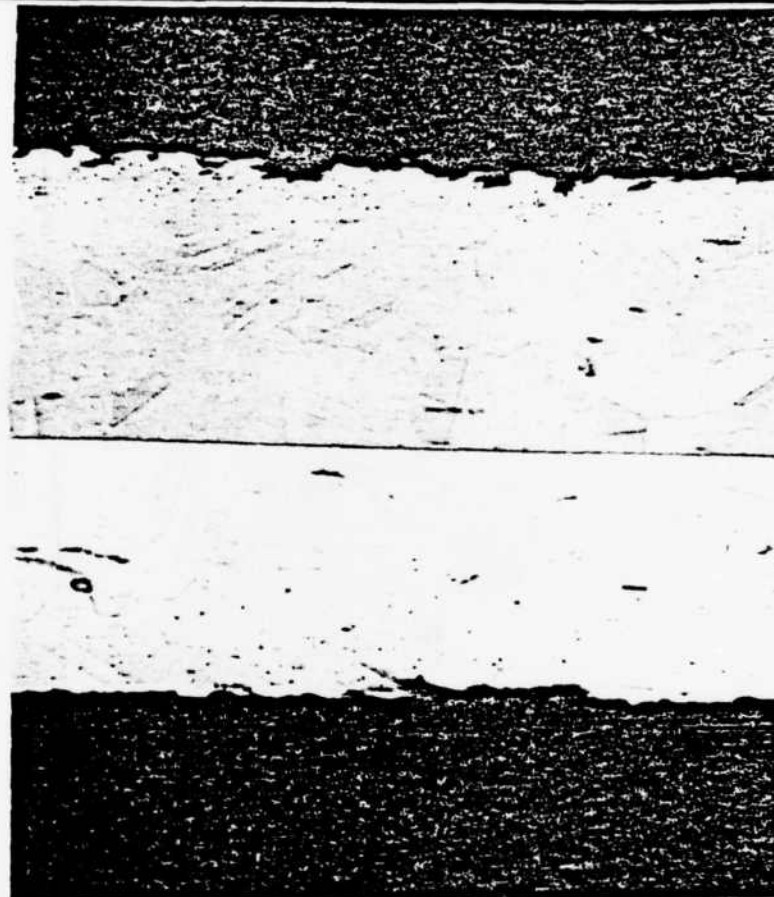
Honeywell

DEVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Study



View A  
Top



View B  
Bottom

FIGURE

34

MA&PE LOG NUMBER

8031

COGNIZANCE

B. Nielson/N. Doddapaneni

ETR NUMBER

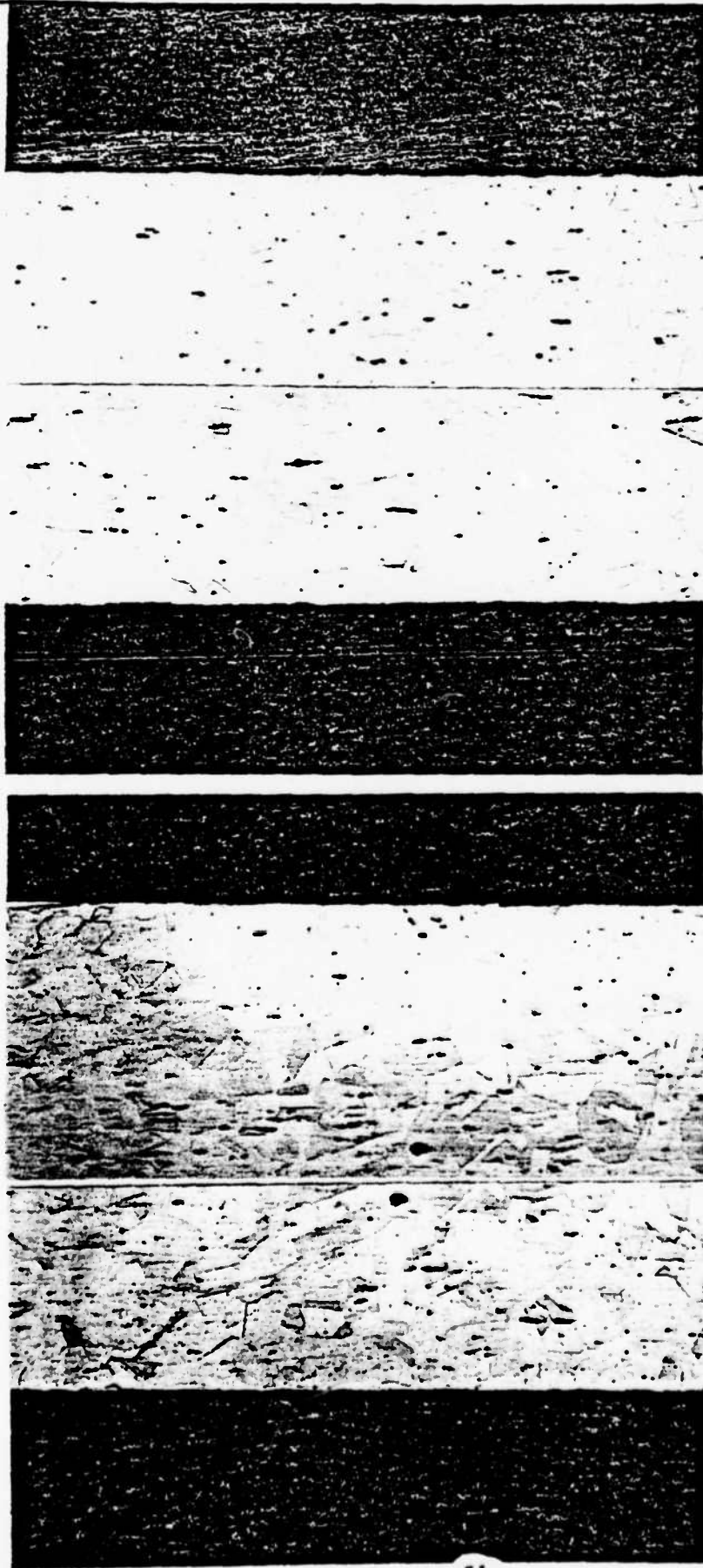
Photomicrographs of Sample B after a seven month exposure to Li/SOCl<sub>2</sub>. Magnification: 575X.

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Honeywell

DEVICE/PART NUMBER

LI/SOCl<sub>2</sub> Safety study



View A  
Top

View B  
Bottom

FIGURE

35

M&PE LOG NUMBER

8031

COGNIZANCE

B. Nielson/N. Doddapaneni

FTR NUMBER

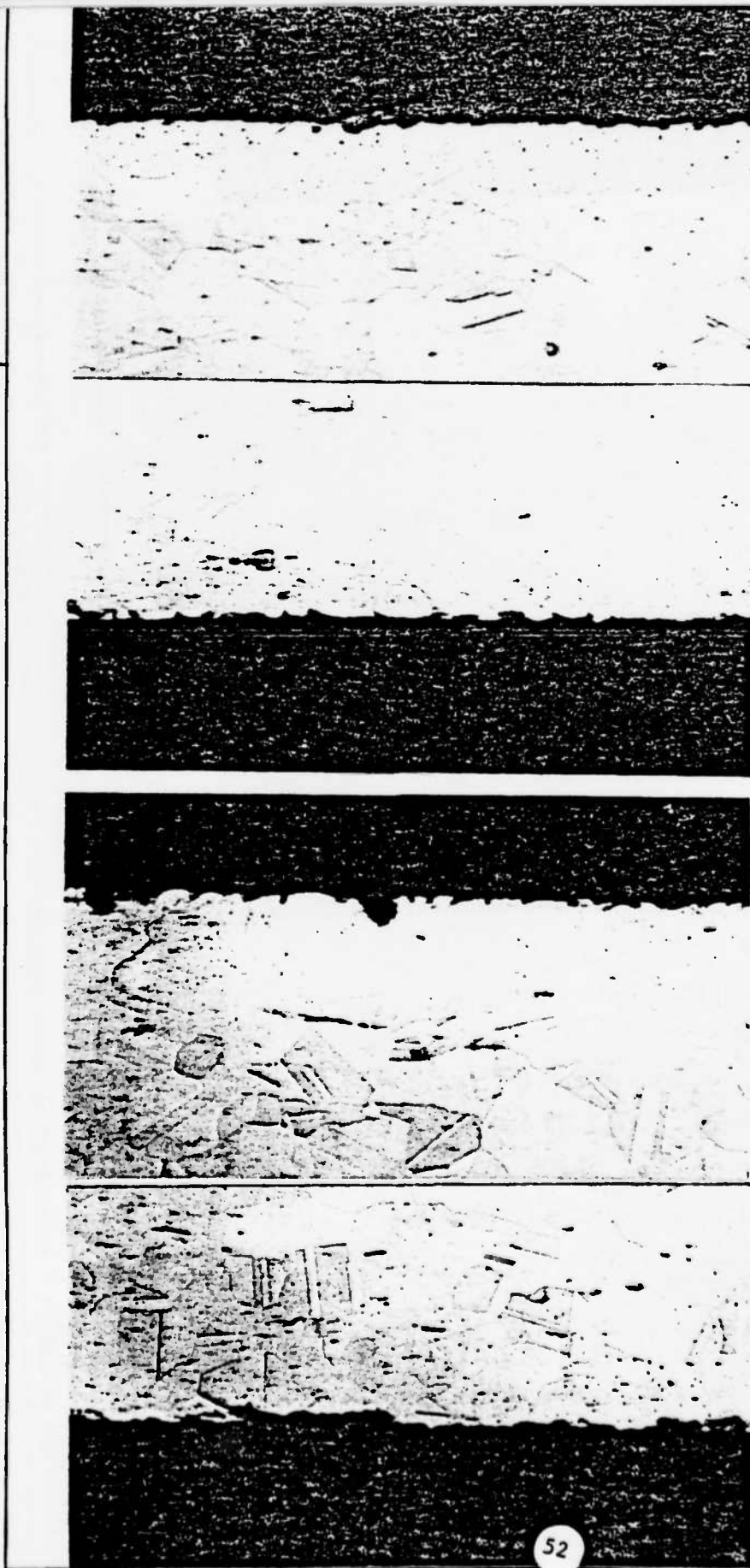
Photomicrograph of Sample C after a seven month exposure to Li/SOCl<sub>2</sub>. Magnification: 575X.

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600 SECOND STREET NE  
HOPKINS, MN 55343

# Honeywell

SERVICE/PART NUMBER

Li/SOCl<sub>2</sub> Safety Study



View A  
Top

View B  
Bottom

FIGURE	36	M&PE LOG NUMBER	8031	COGNIZANCE	B. Nielson/N. Doddapaneni	ETR NUMBER
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Photomicrograph of Sample D after a seven month exposure to Li/SOCl<sub>2</sub>. Magnification: 575X.

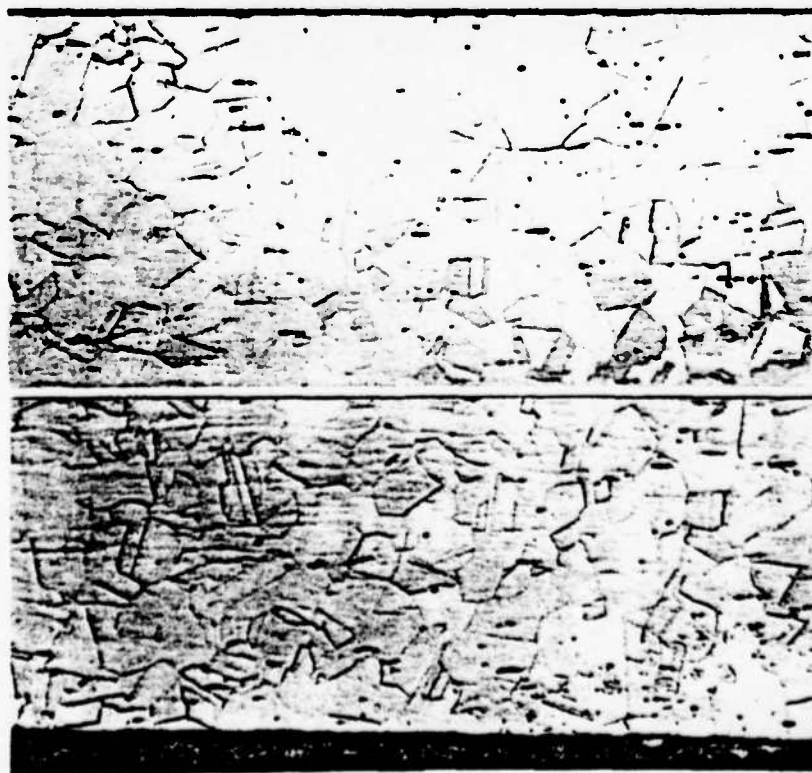


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600 SECOND STREET NE  
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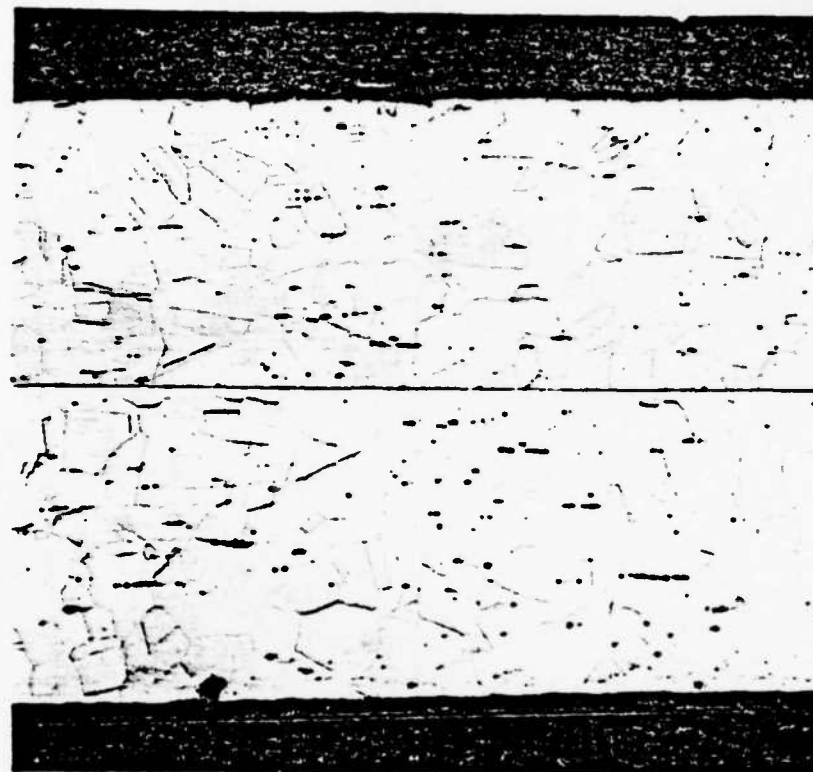
# Honeywell

OFFICE/PART NUMBER

L1/SOCl<sub>2</sub> Safety Study



View A  
Top



View B  
Bottom

53

FIGURE	37	MSPE LOG NUMBER	8031	COGNIZANCE	ETR NUMBER
				B. Nielson/N. Doddapaneni	

Photomicrograph of Sample E after a seven month exposure to Li/SOCl<sub>2</sub>. Magnification: 575X.

DEFENSE SYSTEMS DIVISION  
600 SECOND STREET NE  
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Honeywell

DEVICE/PART NUMBER

L1/SOCl<sub>2</sub> Safety Study



View A  
Top

View B  
Bottom

FIGURE

38

M&PE LOG NUMBER

8031

COGNIZANCE

B. Nielson/N. Doddapaneni

ETR NUMBER

Photomicrograph of Sample F after a seven month exposure to L1/SOCl<sub>2</sub>. Magnification: 575X.

DEFENSE SYSTEMS DIVISION  
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HOPKINS, MN 55343

Honeywell

DEVICE/PART NUMBER

L1/SOC1<sub>2</sub> Safety Study



View A  
Top

View B  
Bottom

FIGURE 39

MAPE LOG NUMBER  
8031

COGNIZANCE  
B. Nielson/N. Doddapaneni

ETR NUMBER

Photomicrograph of Sample G after a seven month exposure to L1/SOC1<sub>2</sub>. Magnification: 575X.



#### 4.0 FORCED DISCHARGE INTO REVERSAL

One of the problems related to a multicell battery is that some of the cells might go into reversal on load and create hazards. The extent of the safety hazard depends on cell design, i.e., anode-limited or cathode-limited. To evaluate the impact of cell design features on safety, spirally wound cells (Figure 40) were built and tested at various discharge and forced overdischarge current densities. Each cell was equipped with a pressure transducer and a valve for activation and for tapping gas samples. Twelve (12) cells were also equipped with internal thermocouples. The glass container was placed in a plastic jacket for protection from flying glass pieces if an explosion was to occur.

There were six types of wrap cells studied:

- Anode-limited cell without catalyst
- Anode-limited cell with  $(\text{CoPc})_n$  catalyst
- Anode-limited cell with FePc catalyst
- Cathode-limited cell without catalyst
- Cathode-limited cell with  $(\text{CoPc})_n$  catalyst
- Cathode-limited cell with FePc catalyst

##### ANODE-LIMITED DESIGN

Anode-limited cells were built with two layers of 0.008" thick lithium foil. Since it was felt that the concentration of LiCl in the discharged cell appears to contribute to the cell behavior under reversal conditions, the cells were built with  $4.88 \pm 0.42$  Ah of theoretical lithium capacity instead of without lithium on the current collector (316L stainless steel). The physical characteristics of the anode-limited cell components were:

<u>Anode</u>	Dimensions:*	1.75" x 3.75" x $(0.011 \pm 0.001)$ "
	No. of Pieces:	2
	Anode Weight:	$1.27 \pm 0.11$ g
	Anode Capacity:	$4.88 \pm 0.42$ Ah
	* For cells 1, 2, 3	1.75" x 3.75" x 0.006"
		Anode Wt. 0.75 g; Capacity 2.89 Ah

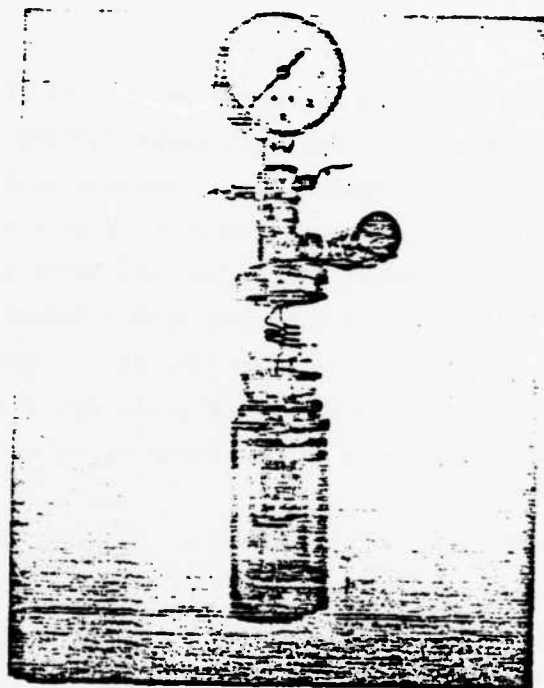


FIGURE 40. LABORATORY CELL FIXTURE TO SIMULATE D-CELL TESTS

Cathode      Dimensions:      1.75" x 3.6" x 0.010" for anode  
Steel                              1.75" x 3.9" x 0.010" for cathode  
Grids

Separators:      Manning Non-Woven Glass Mat  
                            Dimensions: 2" x 8.5" x 0.005"  
                            No. of Pieces/Cell:      4

Electrolyte:      1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>  
                            Amount 17 ml or 20 ml

Attachments:      Pressure Transducer  
                            Pressure Relief Valve  
                            Volume: 3 ml

A total of 18 anode-limited cells were built. The effect of the quantity of lithium and the quantity of electrolyte were tested for cell safety during forced overdischarge into reversal. Cells 1-13 contained 20 ml of electrolyte and cells 14-18 contained 17 ml of electrolyte. All cells were discharged at a constant current of 1 mA/cm<sup>2</sup> (based on cathode area) with diode protection. Each experimental setup consisted of 3 cells connected in a series and discharged and forced overdischarged. The average voltage, discharge time and the cell pressure at the end of 100% depth of discharge to 0.7 volts are given in Table 4. Cells with catalyzed cathodes have higher voltages than cells with baseline cathodes. Cells 12, 15 and 18 contained tetrasulphonated iron phthalocyanine (TsFePc) catalyst. This catalyst is water soluble and therefore can be impregnated easily and efficiently onto the carbon electrode. In the case of the FePc catalyst, which was added to the electrolyte before activation, severe voltage delays were encountered if the activated cells were not subjected to discharge within ten minutes. With TsFePc impregnated cathodes, the voltage delay effects were slightly minimized, however, the cell voltages were lower with TsFePc than with the FePc catalyst.

After discharge to 0.7 volts, the diodes were removed and cells were subjected to forced overdischarge into reversal at various current densities. The cell voltages and the pressures at the ends of the noted depths of discharge at their corresponding current densities are given in Table 5. Cells 1-3, which contained

Table 4. Discharge Performance of Anode-Limited Cells

Cell No.	Catalyst	Rate, mA/cm <sup>2</sup>	Discharge Time to 2.0 V, (Hrs)	Avg. Cell Voltage (volts)	Pressure at 100% DOD, psig
1	-	1	20	3.40	10
2	(CoPc) <sub>n</sub>	1	26	3.50	18
3	FePc	1	30	3.50	6
4	-	1	36	3.38	3 (leak)
5	(CoPc) <sub>n</sub>	1	36	3.50	18
6	FePc	1	35	3.51	3
7	-	1	28	3.38	10
8	(CoPc) <sub>n</sub>	1	28	3.48	18
9	FePc	1	28	3.51	3
10	-	1	21	3.39	11
11	(CoPc) <sub>n</sub>	1	31	3.50	10
12	TsFePc	1	27	3.50	18
13	-	1	40	3.36	10
14	(CoPc) <sub>n</sub>	1	49	3.51	16
15	TsFePc	1	46	3.52	18
16	-	1	35	3.39	10
17	(CoPc) <sub>n</sub>	1	40	3.49	16
18	TsFePc	1	43	3.50	12

Note: Variation in the discharge time is due to variation in the anode thickness.

Table 5. Overdischarge of Anode-Limited Cells into Reversal

Cell No.	Catalyst	Overdischarge Rate (mA/cm <sup>2</sup> )	Cell Voltage, V	DOOO %	Pressure at the End of Overdischarge, psig
1	-	2	-1.2	70	12 <sup>(1)</sup>
2	(CoPc) <sub>o</sub>	2	2.4	30	18 <sup>(1)</sup>
3	FePc	2	5.0	30	39 <sup>(1)</sup>
4	-	5	-4.0	100	20
		10	-5.6	100	98
		20	-4.6	100	180
		30	-3.1	150	220
		5	-4.0	100	46
5	(CoPc) <sub>n</sub>	10	-4.9	100	114
		20	-4.8	100	231
		30	-4.9	150	240
		5	-4.4	100	22
		10	-5.4	100	48
6	FePc	20	-4.1	100	177
		30	-4.2	150	195
		5	-3.9	125	37
		10	-4.5	100	92
		15	-4.7	100	156
7	-	20	-4.5	100	213
		30	-3.7	100	280
		5	-3.3	100	51
		10	-3.5	100	88
		15	-4.2	100	160
8	(CoPc) <sub>n</sub>	20	-4.6	100	280
		30	-9.0	5	320 <sup>(2)</sup>
		5	-4.45	125	23
		10	-5.15	100	70
		15	-5.2	100	121
9	FePc	20	-5.2	100	191
		30	-4.15	100	224
10	-	2	-1.23	53	12
11	(CoPc) <sub>o</sub>	2	-5	53	19.2
12	TsFePc	2	-4.95	53	39.5
13	-	5	-5.5	100	71
		10	-5.6	100	130
		15	-6	100	180
		20	-4.7	100	195
		30	-4.2	100	236
14	(CoPc) <sub>o</sub>	5	Cell failed after 1 hr.	8	>100
15	TsFePc	5	-5.5	100	35
		10	-5.5	Cell fixture shattered after 2 hrs. at 10 mA/cm <sup>2</sup> , at a pressure of 134 psi.	
16	-	5	-5.1	100	72
		10	-6.4	67	150
		5	-4.6	100	70
		10	-6.6	67	136
17	(CoPc) <sub>o</sub>	5	-4.6	100	97
		10	-6.2	67	168
18	TsFePc	5	-4.6	100	97
		10	-6.2	67	168

(1) Forced overdischarge into reversal was stopped before cells vented.

(2) Stopped because of continuous voltage drop.

(3) Test equipment failure forced to disband these cells before venting.

(4) Stopped after 10 mA/cm<sup>2</sup> forced overdischarge because of high cell pressures.

0.75 g of lithium, showed severe voltage drops during forced overdischarge even at 2 mA/cm<sup>2</sup>. Therefore, they were discarded. The abnormal drop in voltage in these cells could be due to electrode stack pressure. Cells 4-18, containing approximately  $1.27 \pm 0.11$  g of lithium on the anode grid, also showed high voltage drops ranging from -4.0 to -7.0 volts.

Cells 14-18, which contained only 17 ml of electrolyte, also showed very high pressures and hence were discontinued. The cause of high pressure buildup could have been due to heat generation in the not-so-flooded cells. Cells 4-13, regardless of cathode type, sustained forced overdischarge current up to 30 mA/cm<sup>2</sup>. During cell reversal, severe heat generation occurred and, therefore, very high pressures were recorded. However, in direct contrast to the cathode-limited cell design (see below under Cathode-Limited Design), the anode-limited design cells under flooded conditions did not vent even after 30 mA/cm<sup>2</sup> overdischarge currents. Typical discharge and forced overdischarge characteristics of anode-limited cells are given in Figures 41-46.

All cells were dismantled immediately after cell reversal. Temperatures of more than 100°C were measured in the open electrode stack in all cells. The actual temperature during cell reversal studies, therefore, could be much higher than 100°C as measured in the open electrode stacks.

#### CATHODE-LIMITED DESIGN

Cell reversal studies with cathode-limited design were conducted in order to assess the design impact on safety. Cells tested consisted of baseline cathode, (CoPc)<sub>n</sub> catalyzed cathodes and FePc catalyzed cathodes. Cathode-limited wrap cells were first discharged with diode protection and after removing diode, then forced overdischarged into reversal. Each experimental setup consisted of 3 cells connected in series during both discharge and reversed overdischarge. The physical characteristics of the cathode-limited cell components were:

Anode - Two pieces of lithium sandwiched on grid.  
Dimensions: 1.75" x 3.75" x 0.020" (two pieces)  
Weight: 2.35 g  
Capacity:  $2.35 \times 3.86 = 9.07$  Ah



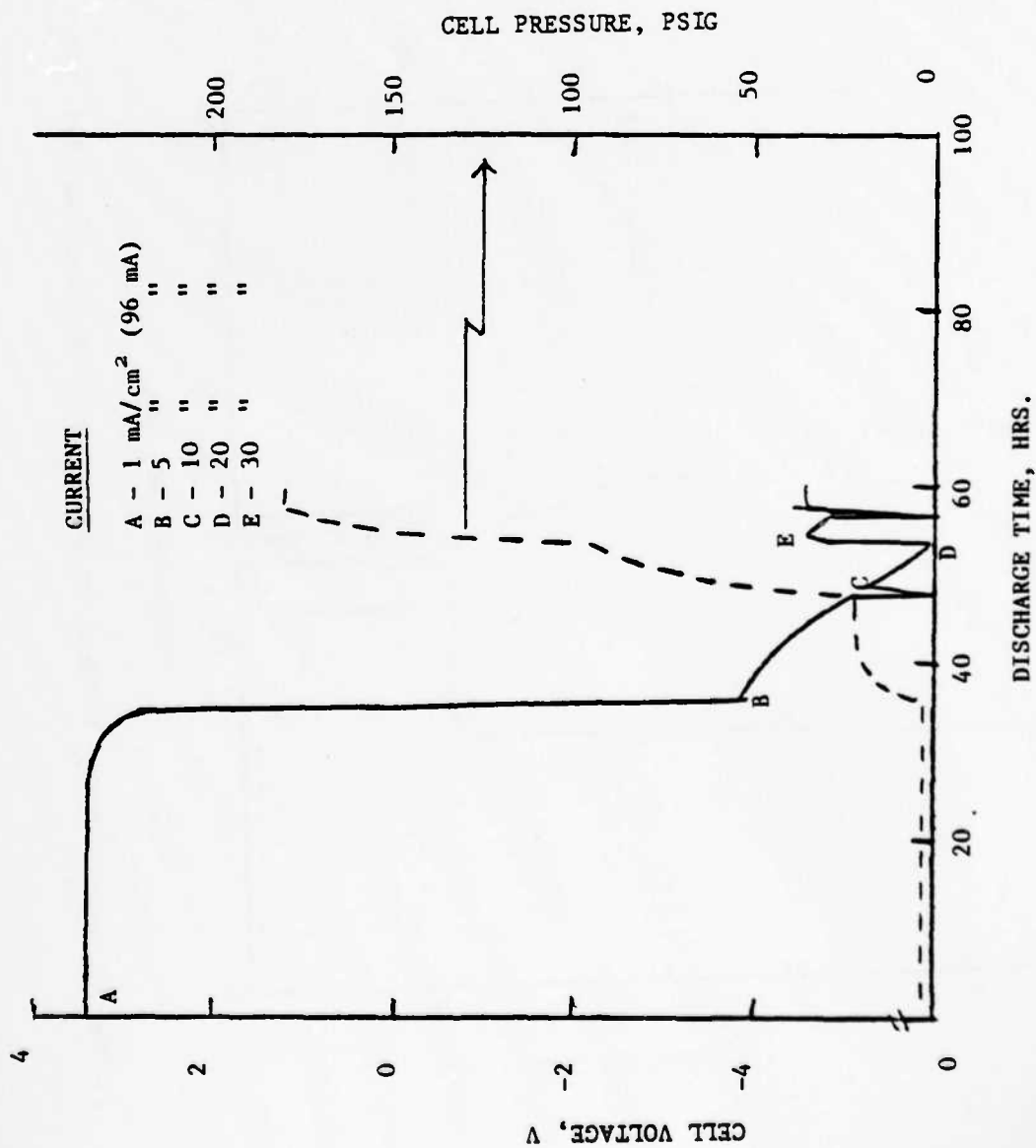


FIGURE 41. DISCHARGE AND REVERSAL OF A BASELINE, ANODE-LIMITED LAB WRAP CELL CONTAINING 1.25 g OF LITHIUM.

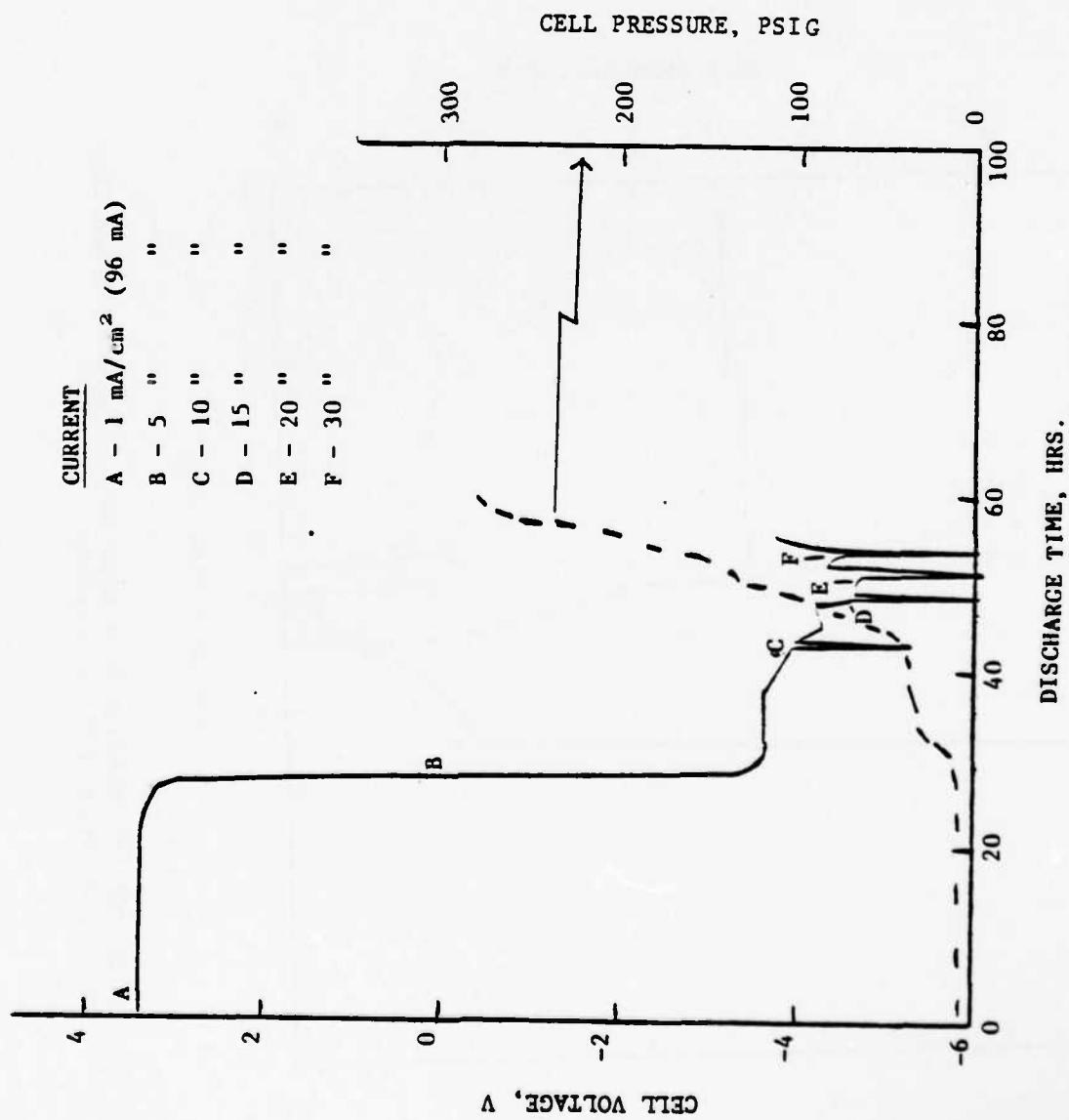


FIGURE 42 . DISCHARGE AND REVERSAL OF ANODE-LIMITED BASELINE LAB WRAP CELL.

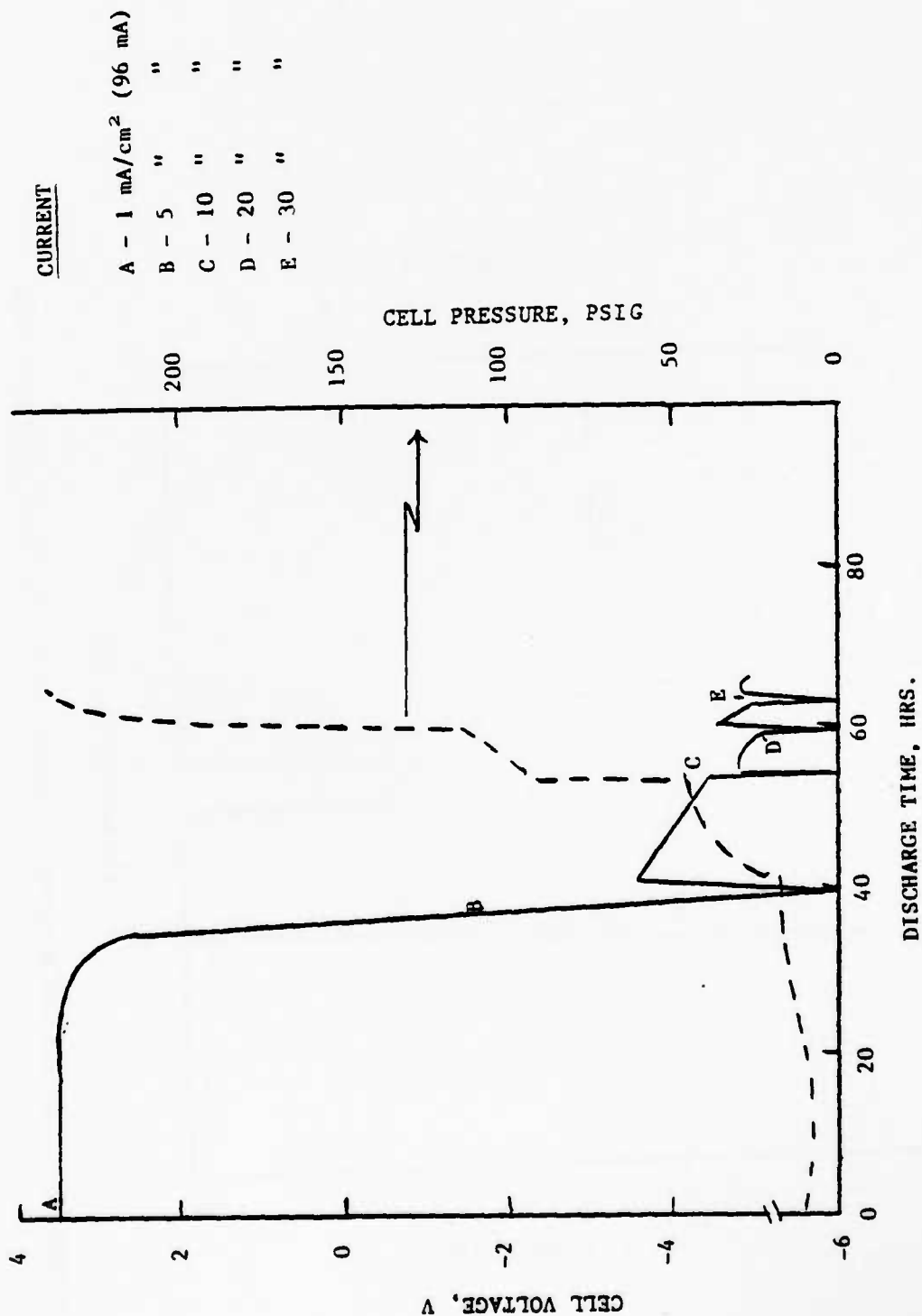


FIGURE 43. DISCHARGE AND REVERSAL OF 7% (CoPc)<sub>n</sub> ANODE-LIMITED LAB WRAP CELL CONTAINING 1.25g OF LITHIUM.

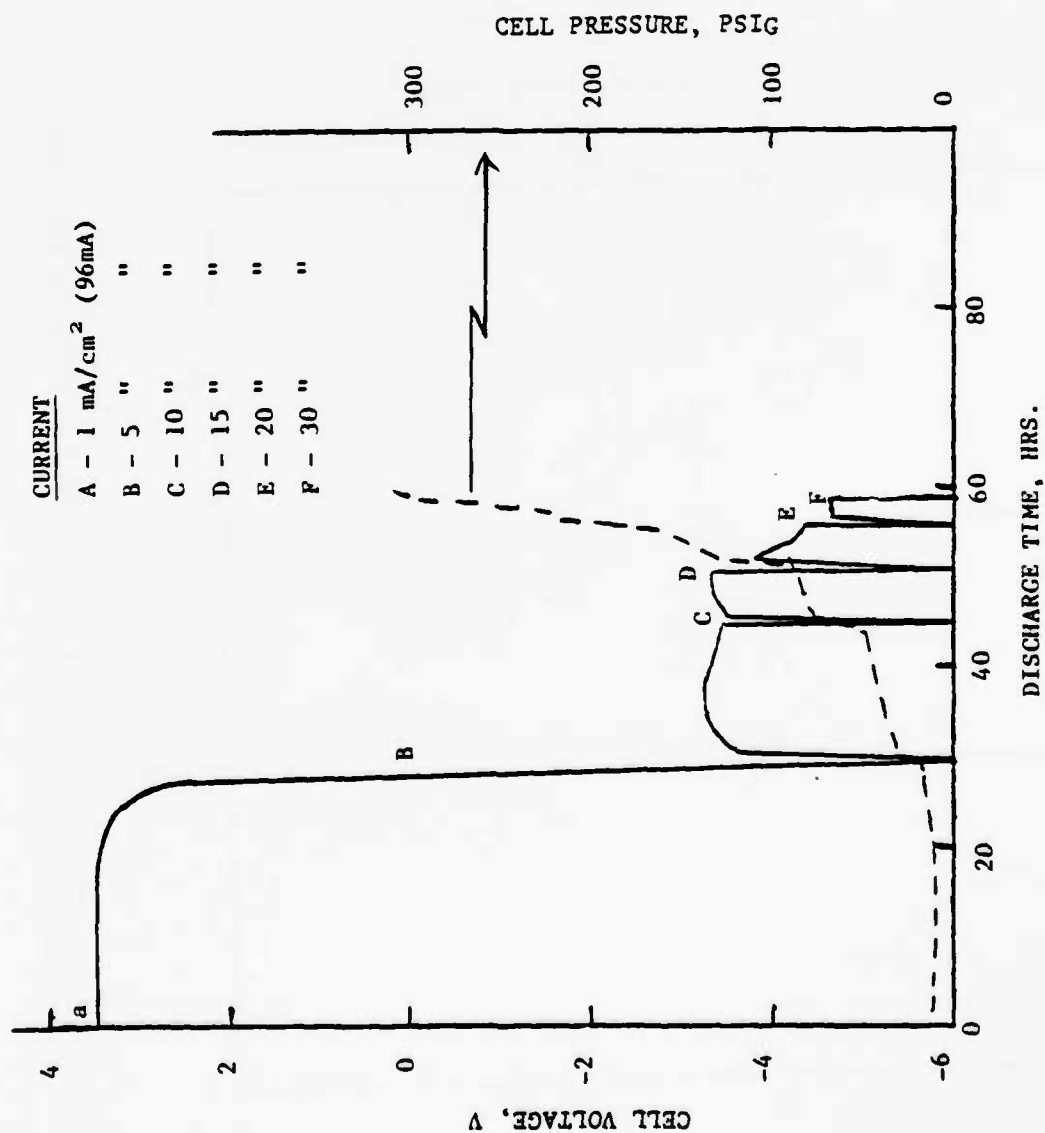


FIGURE 44. DISCHARGE AND REVERSAL OF ANODE-LIMITED, 7% (CoPc)<sub>n</sub> LAB WRAP CELL.

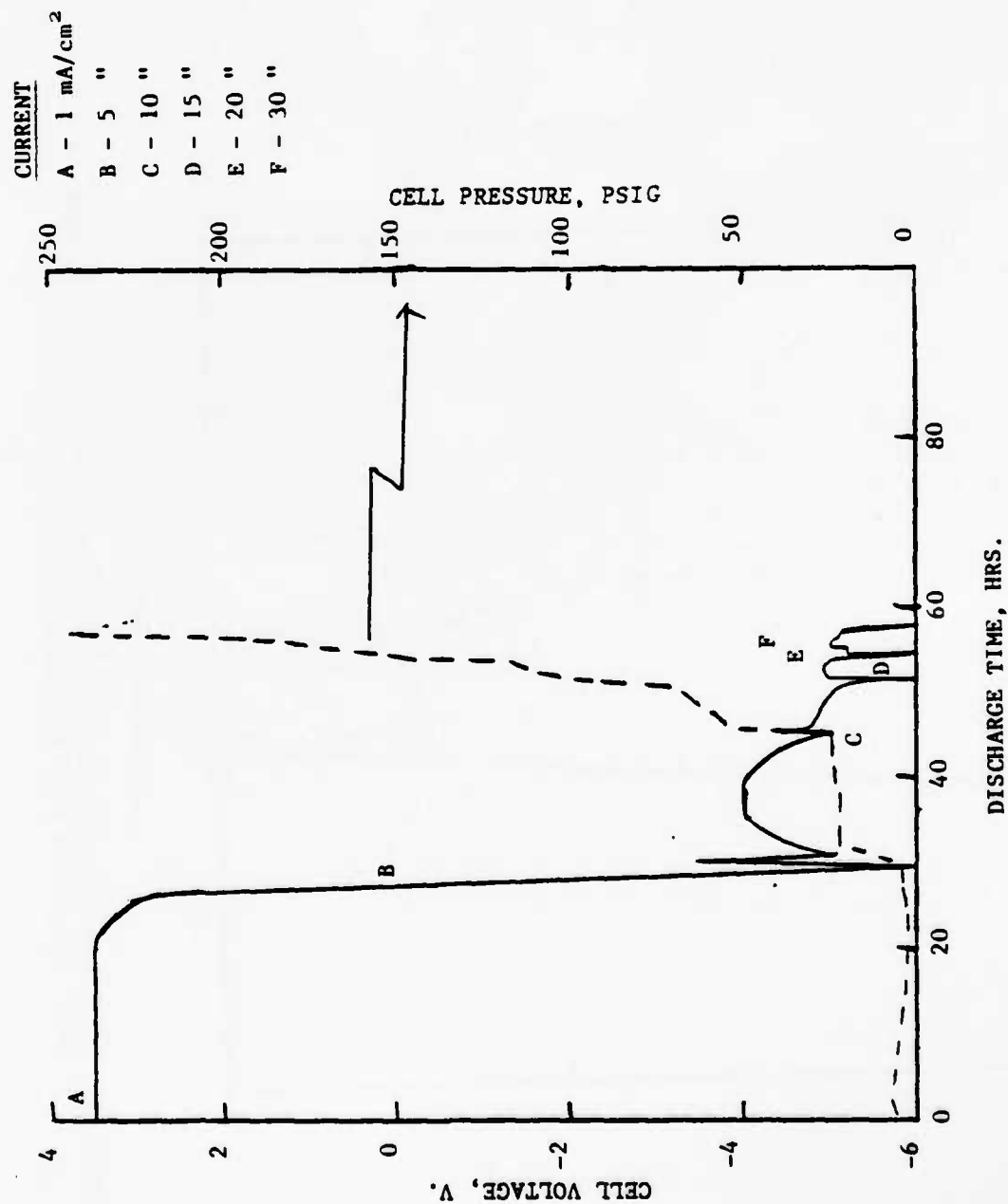


FIGURE 45. DISCHARGE AND REVERSAL OF ANODE-LIMITED, FePc LAB WRAP CELL.



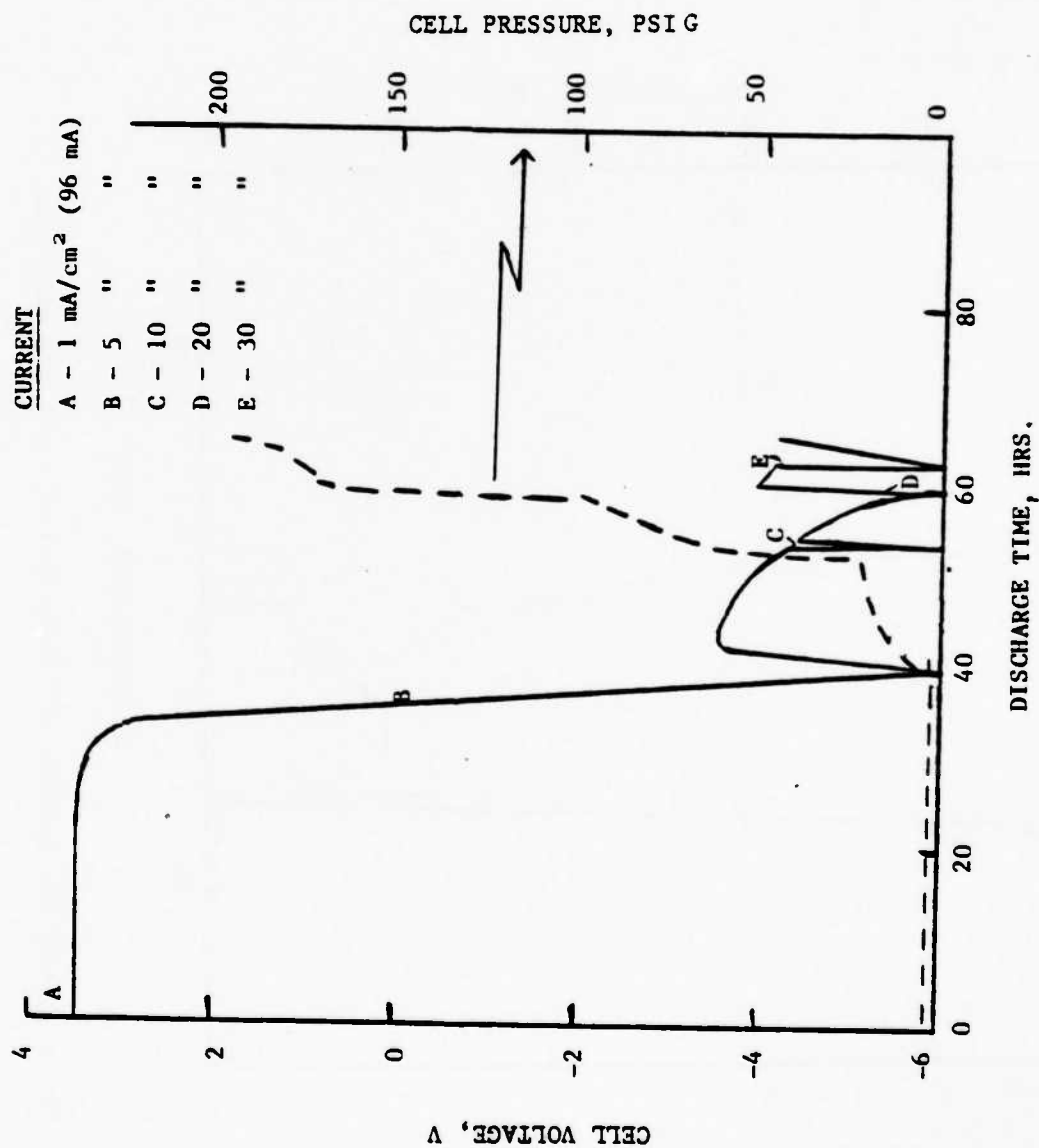


FIGURE 46. DISCHARGE AND REVERSAL OF 1.5% TsFePc, ANODE-LIMITED, LAB WRAP CELL CONTAINING 1.25 g OF LITHIUM.

### Cathode

Dimensions\*: 1.75" x 4.5" x 0.040" (first piece)  
1.75" x 4.0" x 0.040" (second piece)  
Area: 96.0 cm<sup>2</sup>  
Volume: 9.75 ml  
Weight: 3.7 - 3.9 g  
Void Space: 81.85% baseline cathode  
(i.e., 0.8185 x 9.75 = 7.98 cc)  
82% (CoPc)<sub>n</sub> cathode  
(i.e., 0.81 x 9.75 = 7.90 cc)

### Stainless Steel Grids

Dimensions: 1.75" x 3.6" x 0.010" for anode  
1.75" x 3.9" x 0.010" for cathode

### Separators - Manning Non-Woven Glass Mat

Dimensions: 2.0" x 8.5" x 0.005"  
No. pieces used/cell: 4  
Volume: 2.786 ml  
Porosity: 90%  
Void Space: 0.9 x 2.786 = 2.51 cc

### Electrolyte - 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>

Amount: 20 ml/cell

### Cell Case - Compatibility Glass Tube

Volume: 32 ml

- \* Cells 19-21, Cathodes = 1.75" x 5.25" x 0.04" (First piece)  
1.75" x 4.5" x 0.04" (Second piece)  
Area = 110 cm<sup>2</sup>  
Anode = 1.75" x 4.25" x 0.020" (Two pieces)  
Dimensions of separators and grids were also changed accordingly.

### Attachments

Thermocouple (For 12 cells only)

Pressure Transducer

Pressure Relief Valve

Volume: 3 ml

A total of 27 cathode-limited cells with the above electrode design and tested. The cells were discharged at constant current of 1 mA (#29-30 at 5 mA/cm<sup>2</sup>) with diode protection. The discharge voltage the pressure of cells without thermocouple (Cell #19 to 33) at the 100% depth of discharge to 0.7 volts is given in Table 6. Slight in cell-to-cell voltages were observed. This is attributed to the treatment and storage conditions. The average discharge voltage for baseline cathode, 3.48 V for (CoPc)<sub>n</sub> catalyzed cathode and 3 catalyzed cathode. The discharge time at 1 mA/cm<sup>2</sup> was 60 hours 71 hours for (CoPc)<sub>n</sub> catalyzed cells and 57 hours for FePc catalyst. FePc catalyst does not improve life at 1 mA/cm<sup>2</sup> rate but does at 5 mA/cm<sup>2</sup> for this behavior is that FePc undergoes decomposition on longer SOCl<sub>2</sub>. Because of the catalytic ability of FePc to improve cell the achieved power is still higher at the low rate discharge. FePc catalyst seems to modify the reaction mechanism whereby no gas is formed. This results in lower cell pressure.

After discharge to 0.7 V, the diodes were removed and cells were forced overdischarge into reversal at various rates. Their data is in Table 7. Cells 19-21 showed erratic behavior during forced overdischarge. Three cells differed from the other cells in that they had more electrode stacks. The behavior of other cells with reduced electrode stacks to be identical with and without electrolyte insoluble (CoPc)<sub>n</sub> catalyst. They sustained forced overdischarge current density of 20 mA/cm<sup>2</sup> at 100% depth of discharge time. However, FePc catalyzed cells sustained a current density of 30 mA/cm<sup>2</sup> during forced overdischarge.

Table 6. Discharge Performance of Cathode-Limited Cells

Cell #	Catalyst	Rate, mA/cm <sup>2</sup>	Discharge Time to 2.0 V, (Hrs)	Cell Volt Voltage	Pressure 100% DOD
19*	-	1	57	3.36	-
20*	(CoPc) <sub>n</sub>	1	74	3.38	20
21*	-	1	57	3.02	16
22	(CoPc) <sub>n</sub>	1	73	3.30	31
23	FePc	1	58	3.50	16
24	-	Mechanical Failure			
25	-	1	66	3.37	16
26	(CoPc) <sub>n</sub>	1	65	3.10	24
26	(CoPc) <sub>n</sub>	1	73	3.47	17
28	-	1	60	3.06	14
29	-	5	8.6	3.02	7
30	FePc	5	11.2	3.28	6
31	-	1	65	3.38	23.5
32	FePc	1	56	3.53	15
33	(CoPc) <sub>n</sub>	1	71	3.48	14

\* Contained only one layer of separator and a longer electrode stack.

Table 7. Forced Overdischarge of Cathode-Limited Cells Into Reversal

Cell #	Catalyst	Overdischarge Rate (mA/cm <sup>2</sup> )	Cell Voltage, V	DOOD, %	Pressure at the End of Overdischarge, psig	Remarks
19	-	0.5	-1.10	105	TEF	Leak
		1.0	-1.2	91	"	"
		2.0	-1.2	100	"	"
		5.0	-1.5	100	"	"
20	(CoPc) <sub>n</sub>	0.5	-1.2	50	39	Cell voltage, erratic, discontinued
21	-	0.5	-1.2	150	30	Cell voltage, erratic, discontinued
22	(CoPc) <sub>n</sub>	5.0	-1.36	200	64	Cell vented
		5.0	-1.36 → 5.0	12	>100	
23	TsFePc	5.0	-1.16	500	43	
		10.0	-1.4	400	48	
		15.0	-1.8	200	61	
		20.0	-1.3	500	96	
		20.0	-1.3 → -5.0	5	>100	
25	-	5.0	-0.2	200	47	Cell vented
		10.0	-0.6	1100	108	
		15.0	-1.0	100	120	
		15.0	-1.0 → -5.0	10	>150	
26	(CoPc) <sub>n</sub>	5.0	-2.4	72	52	Stopped before voltage dropped below -7.0V
		7.0	-3.5	280	65	
		10.0	-4.3	360	>100	
27	(CoPc) <sub>n</sub>	5.0	-0.10	170	25	Forced overdischarge discontinued when voltage dropped below -5.0V
		10.0	-0.15	550	32	
		15.0	-0.20	600	36	
		20.0	-0.32	720		
		20.0	-0.32 → -5.0	320	100	
28	-	1.0	-0.35	50	23	Forced overdischarge discontinued
		10.0	-0.76	700	33.5	
		15.0	-1.05	800	42	
		20.0	-1.40	1280	47.5	
29	Wee disassembled after discharge and analyzed for electrochemically consumed lithium					
30	" "	" "	" "	" "	" "	
31	-	10.0	-0.5	100	31	Discontinued
		20.0	-1.2	720	45	
		20.0	-1.2 → -6.0V	580	>180	
32	FePc	10.0	-0.3	100	35	Cell exploded
		20.0	-0.6	1100	75.5	
		30.0	-1.0	100	>280	
33	(CoPc) <sub>n</sub>	10.0	-0.55	100	21	Voltage dropped below -5.0V
		20.0	-1.10	200	>100	

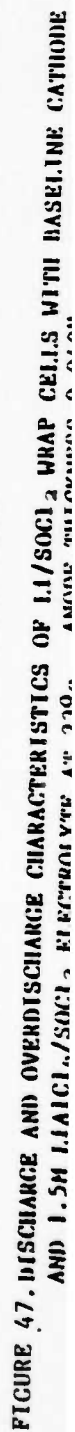
\* Depth of Overdischarge



The cell pressure increases slightly (except for FePc cells) during discharge and the increase accelerates for all cells when overdischarged and depends upon the rate. Cell failure was usually accompanied by a spontaneous spike in pressure beyond 200 psig and sharp voltage drop.

All cells were postmortemed after overdischarge. It was noticed that at the end of overdischarge, lithium was completely consumed leaving bare stainless steel grids. The products formed during cell reversal seem to react with lithium. It is interesting to note that this finding contradicts the reported data in which it was reported that lithium either deposits or intercalates with carbon in the cathode during cell reversal. Our data show that free lithium does not exist probably due to its consumption by chemical reactions with cell reversal products.

In order to further examine the thermal behavior of cathode-limited cells during discharge and forced overdischarge into reversal, wrap cells were built with thermocouple, pressure transducer and vent valve. The temperature of the cell at the center of the wrap was measured with an Omega type-T thermocouple. In Figures 47-52, the temperature, pressure and voltage behavior of wrap cells are presented. Irrespective of cathode types [i.e., undoped cathode, FePc or (CoPc)<sub>n</sub> doped cathodes], the cells either exploded or vented under forced overdischarge current rate of 30 mA/cm<sup>2</sup> after 1-5 hours. The cell failure is preceded by a sudden increase in both temperature and pressure. The temperature, pressure and voltage behavior of these cells six to seven minutes prior to the cell failure are given in Figures 53-56. All have shown similar characteristics. It can be concluded that the thermal runaway conditions are created during cell reversal. Further, the current density and cell design appear to influence the thermal behavior. Even in the case of the cathode-limited design, the amount of lithium left after discharge seems to influence the cell safety as shown in Figures 57 and 58. The low sustaining current rate capability of these cells might be due to depletion of lithium at an early stage and therefore drop in voltage causing severe heat generation. However, the anode-limited cells experienced higher temperatures without causing cell explosion.



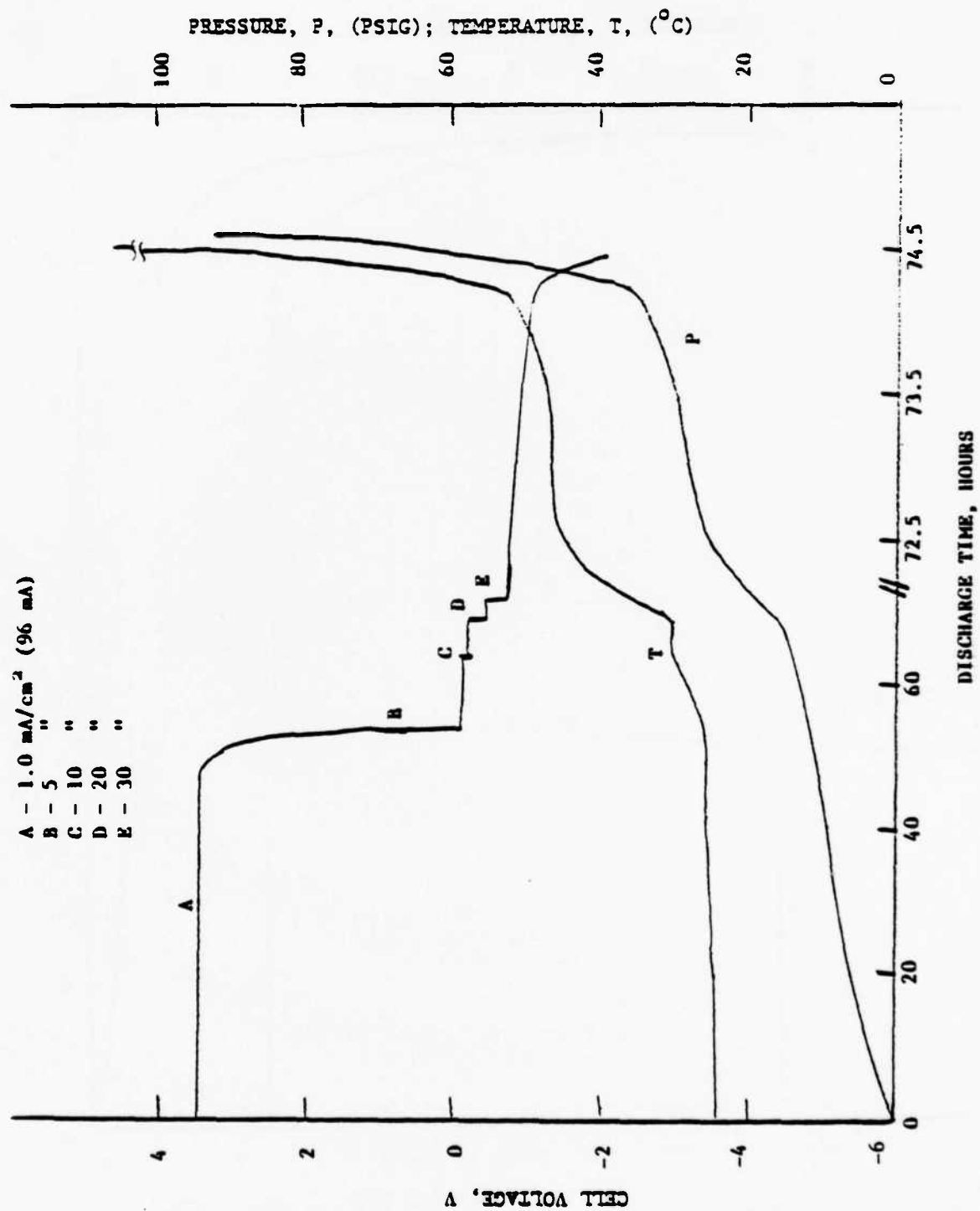


FIGURE 48. DISCHARGE AND OVERDISCHARGE CHARACTERISTICS OF  $\text{Li/SOCl}_2$  WRAP CELLS WITH  $\text{CoPc}$  CATHODE

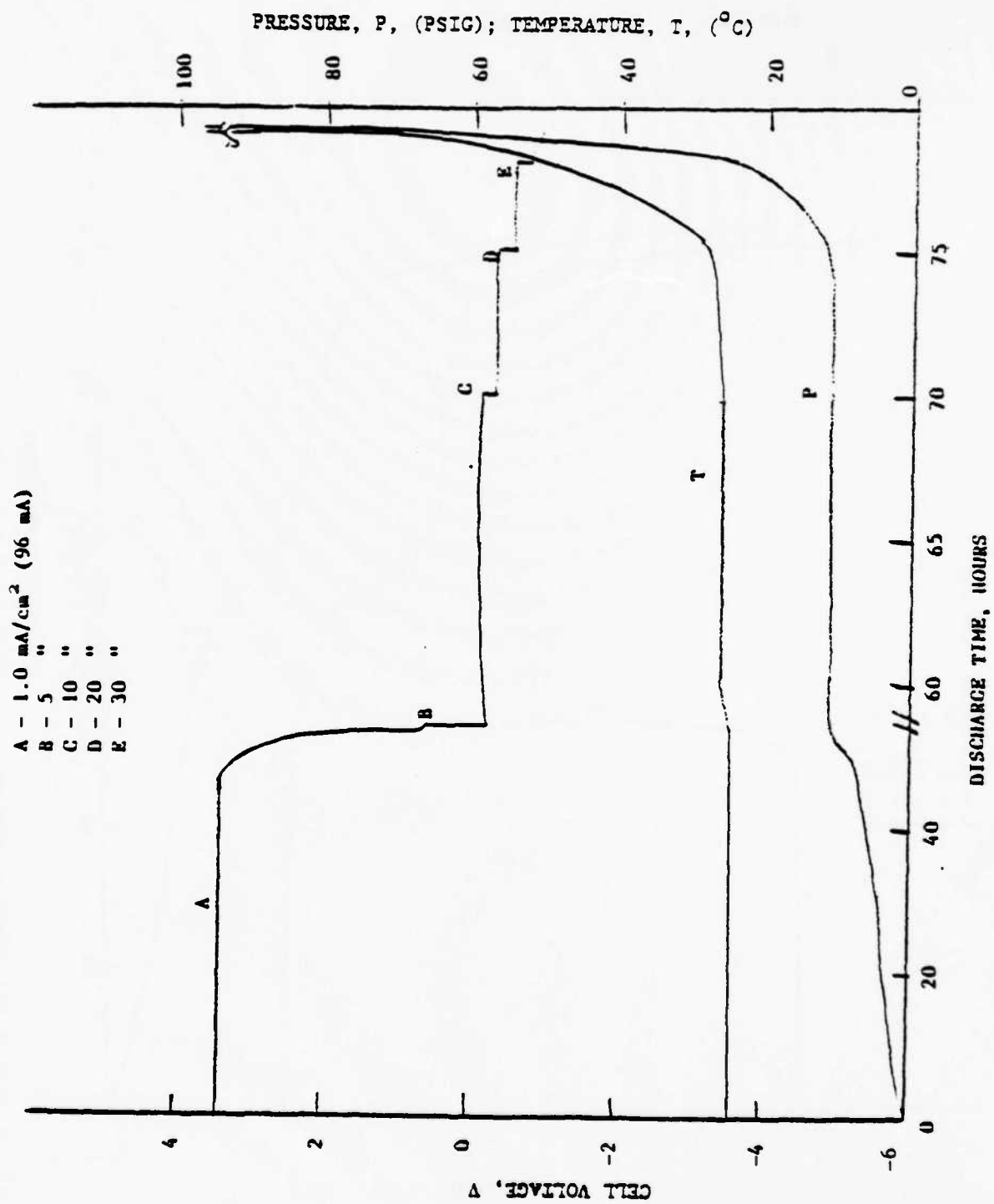
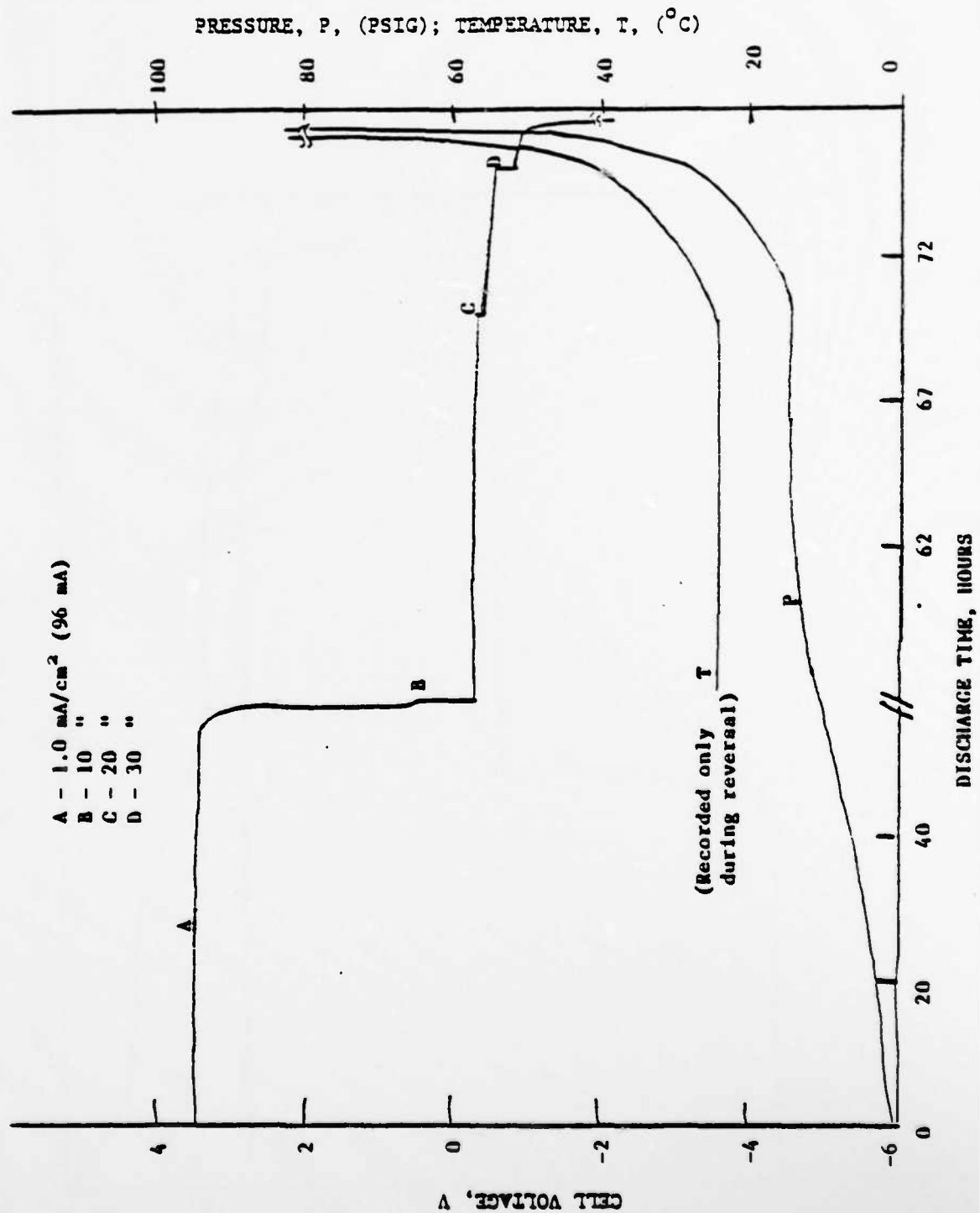
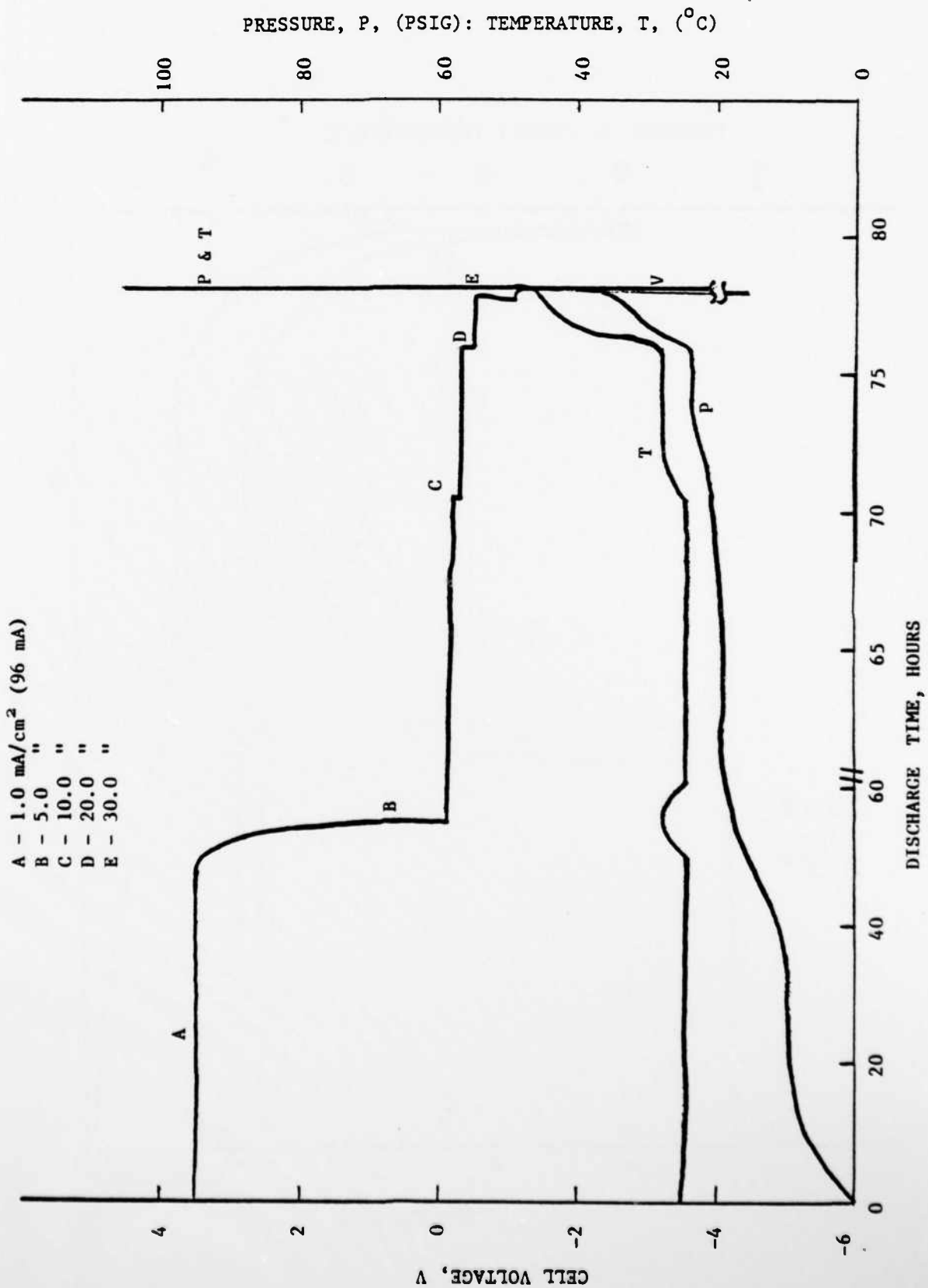
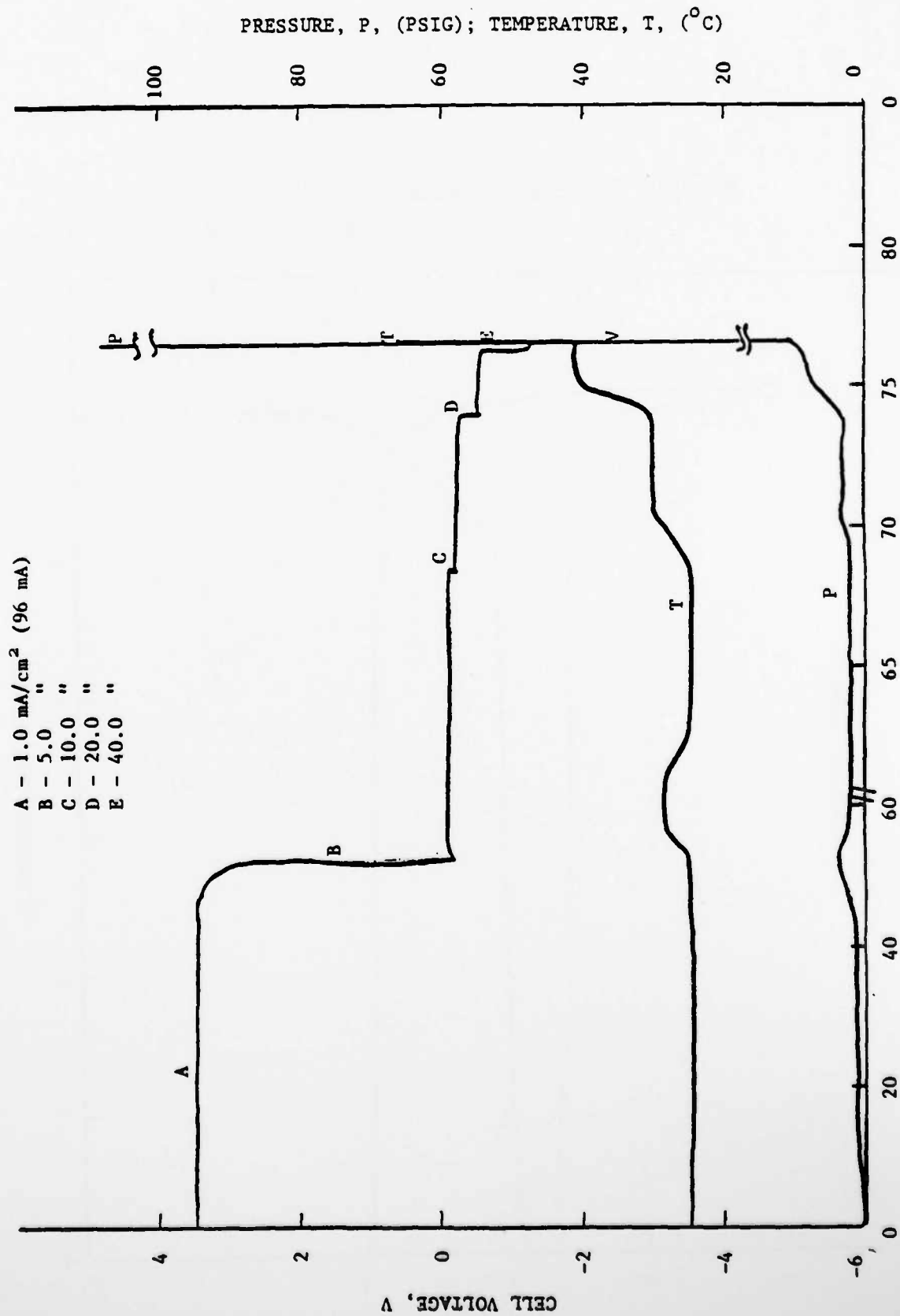


FIGURE 49. DISCHARGE AND OVERDISCHARGE CHARACTERISTICS OF  $\text{Li}/\text{SOCl}_2$  WRAP CELLS WITH  $(\text{Co})\text{C}$  CATHODE









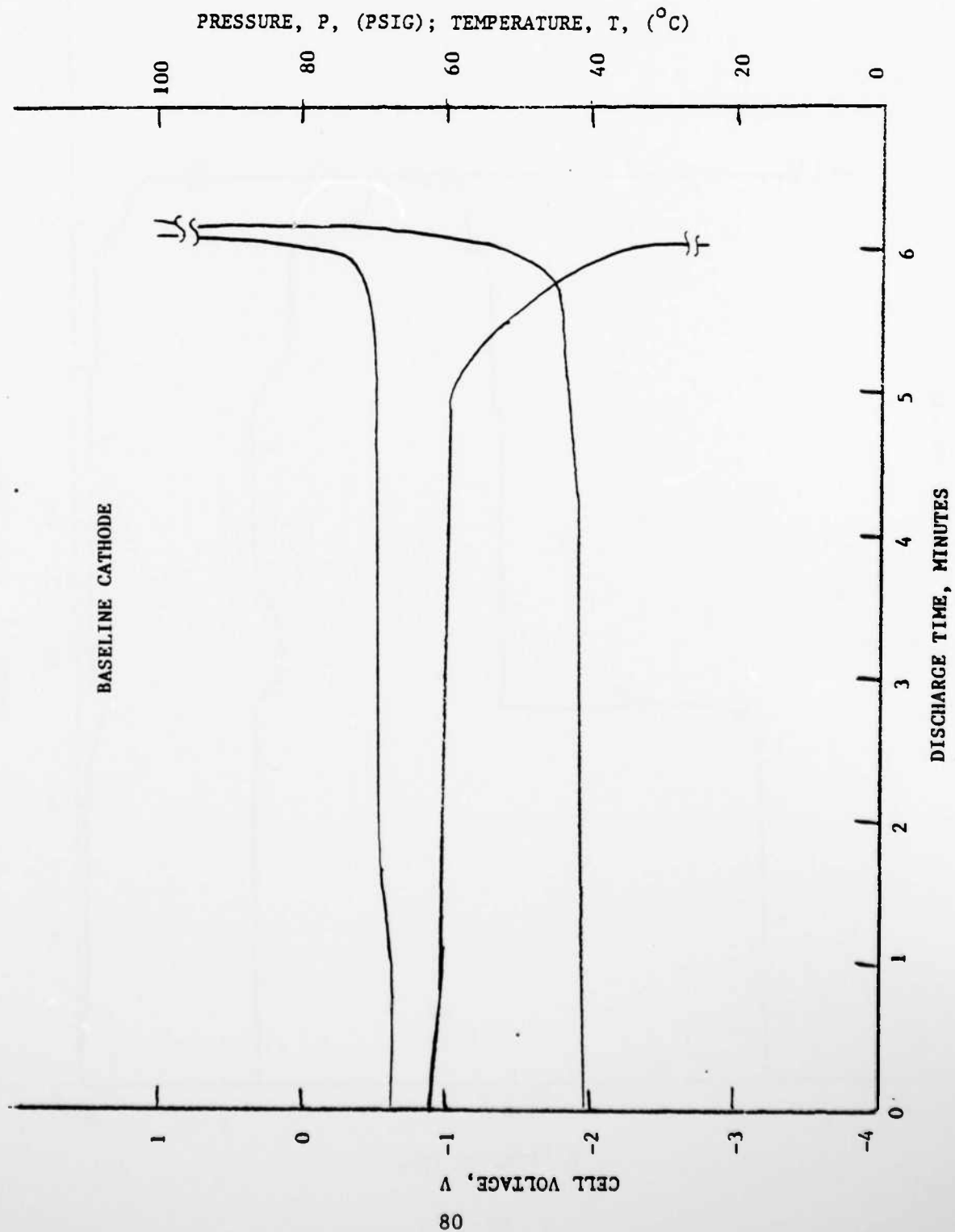
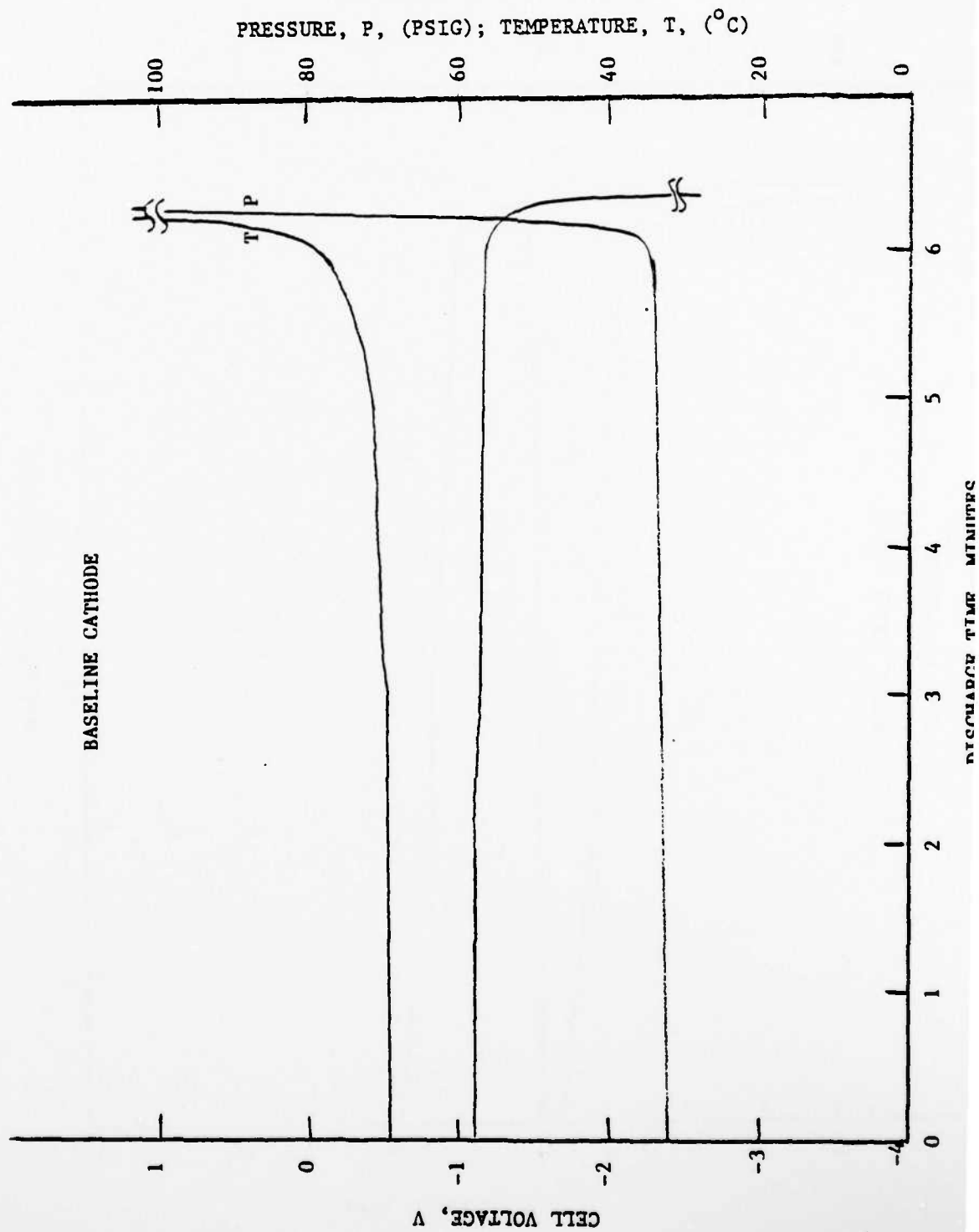
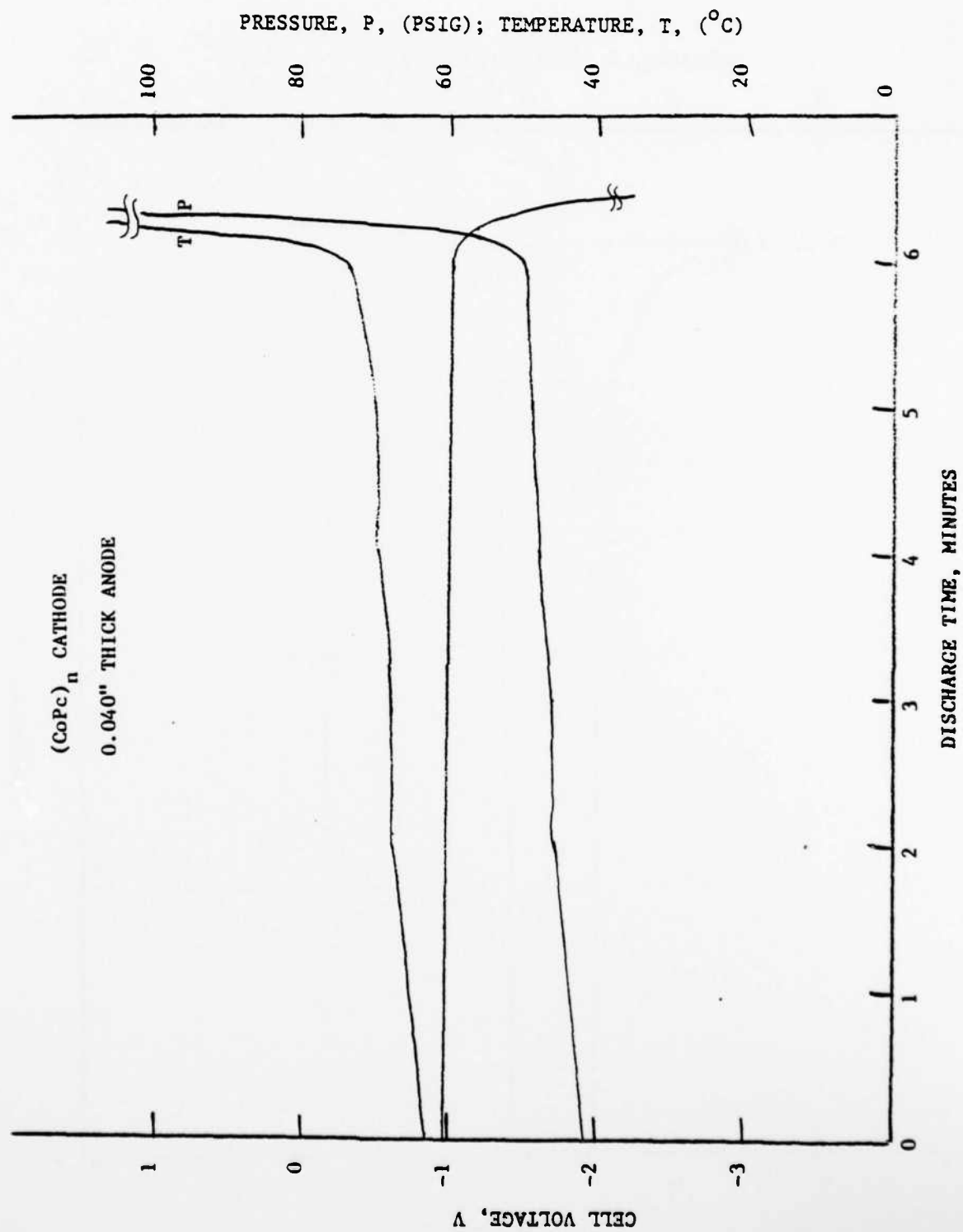
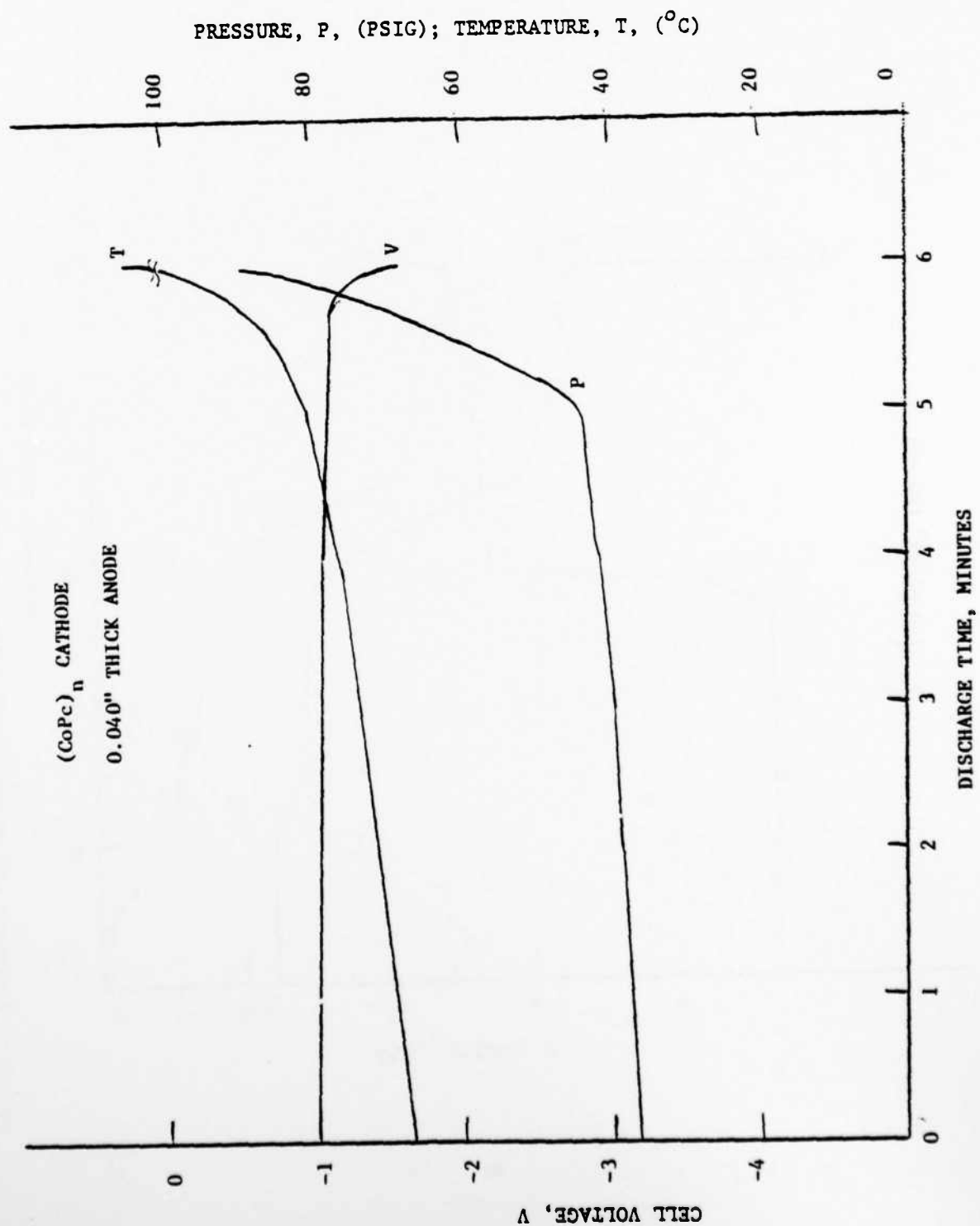
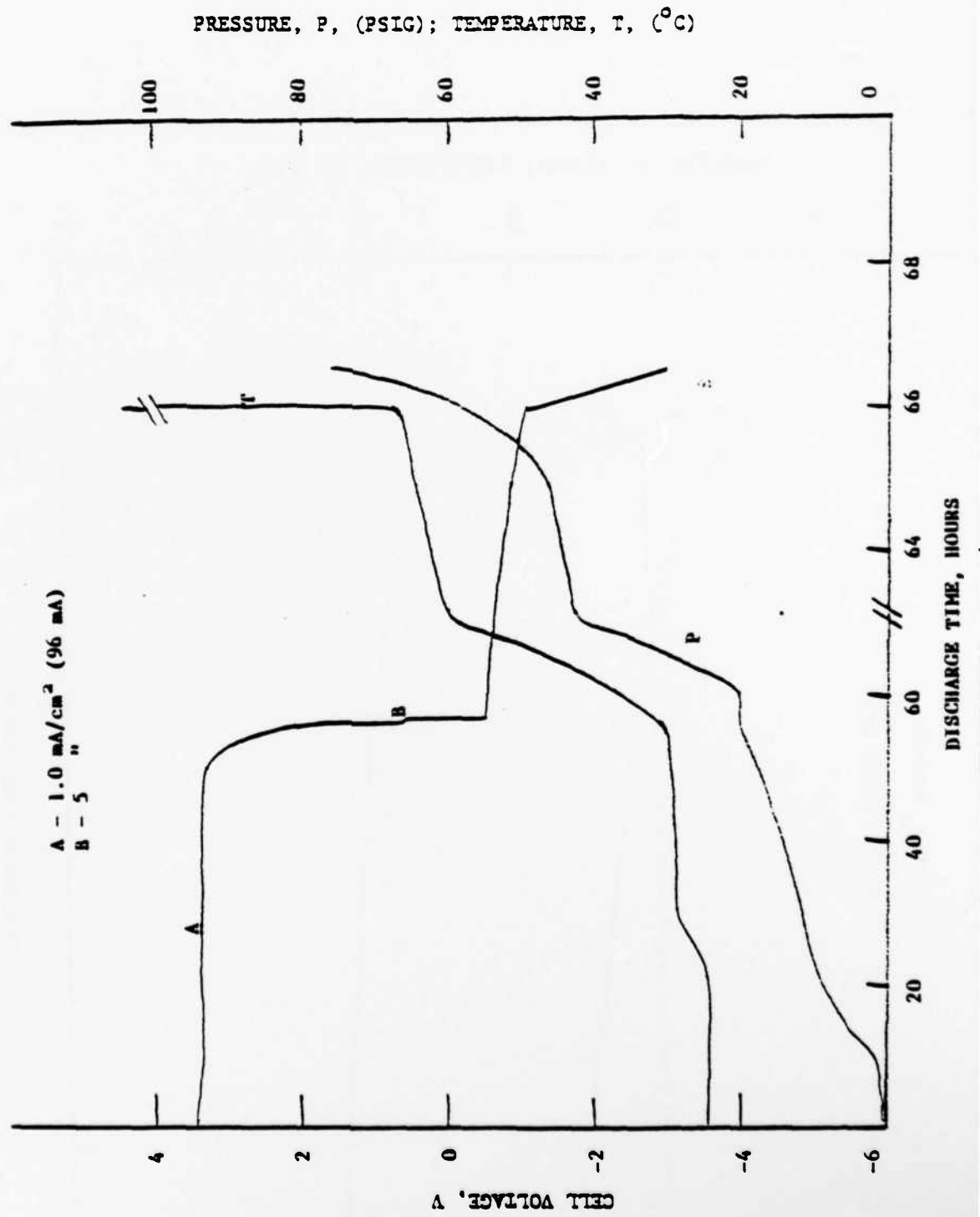


FIGURE 53. VOLTAGE, PRESSURE AND TEMPERATURE BEHAVIOR OF 11/2001 UNDER CHARGE DURING DISCHARGE

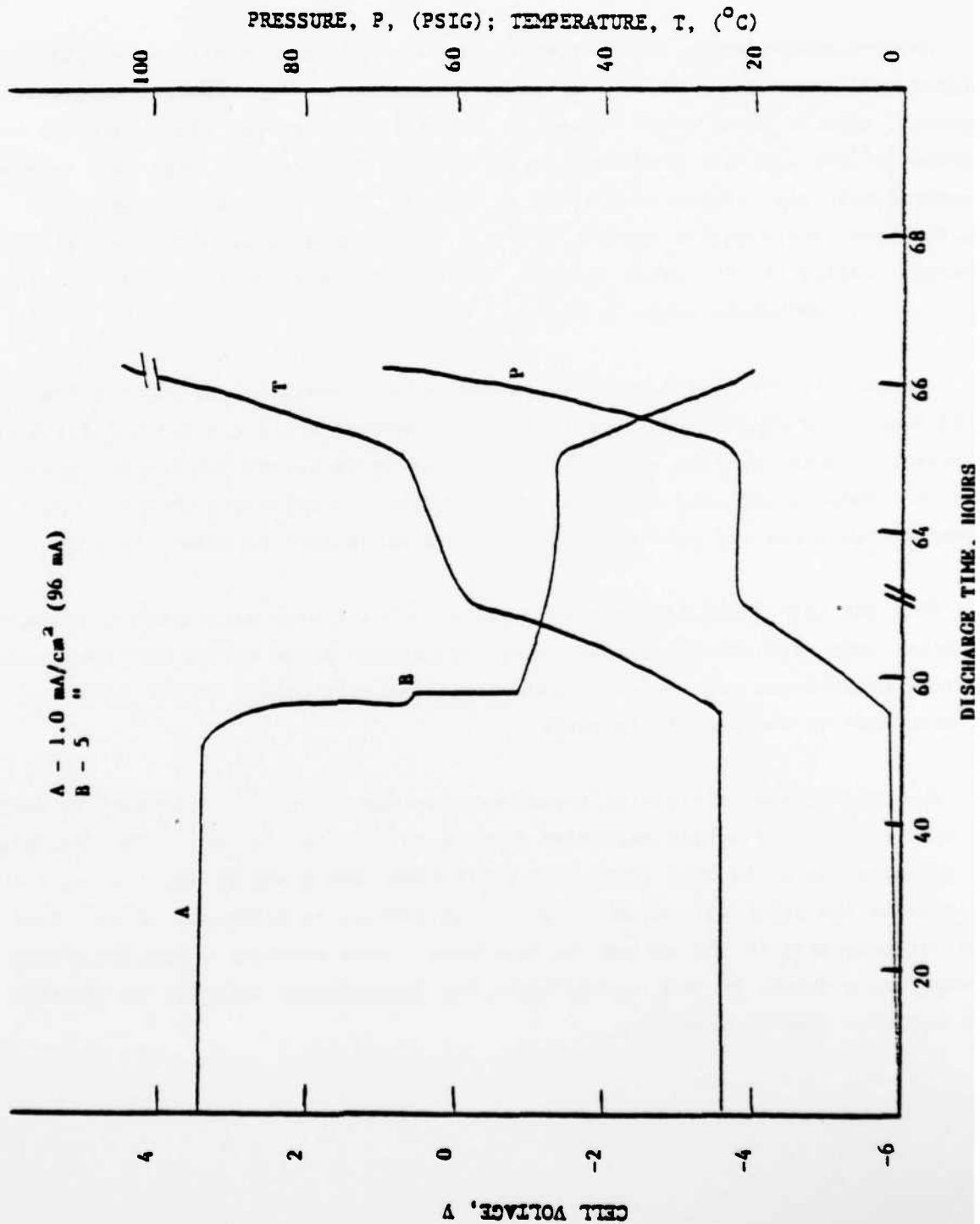












In summary, it can be said:

- Anode-limited design cells experienced severe heat generations leading to higher cell pressures even at low current densities during reversal studies. However, none of these cells vented or exploded. Postmortem after reversal studies showed lithium dendrite formation on the cathode surface. At high cell reversal temperatures, the lithium dendrites, if formed, could be consumed chemically. Furthermore, the reactive species produced under these conditions could also undergo changes leading to new stable species. Therefore, care should be taken to interpret the reaction mechanism based on analysis of products.
- Cathode-limited design cells sustained current densities up to 20 mA/cm<sup>2</sup> for 100% depth of overdischarge into reversal. However, all cells exhibited sudden increase in both pressure and temperature leading to either venting or explosion. The cell failure appeared to be related to thermal runaway conditions. Both chemical reactions and cell shorting could cause unexpected safety hazards.
- When the cathode-limited design cells were built with only slightly excessive lithium, they were able to sustain very low current rates during cell reversal. Further experiments are needed to understand the cell safety on the amount of lithium left at the end of discharge.
- The product analysis during forced overdischarge into cell reversal is needed to understand the reaction mechanism leading to the cell failure. The analysis of products has to be done throughout the forced overdischarge into reversal to examine the critical concentration of the product or products, if any, that are participating in the exothermic reactions. Cell reversal of anode-limited design cells should be done at low operating temperatures in order to identify the unstable species produced.

## 5.0 MISCELLANEOUS STUDIES

### ELECTROCHEMICAL

Elucidation of kinetic and reaction mechanisms of thionyl chloride reduction with and without electrocatalysts such as CoPc, and FePc is important to understand the role of intermediates and/or final products. It was shown that CoPc and FePc not only catalyze the electrochemical reduction rate of  $\text{SOCl}_2$  but also modify the reaction mechanisms. In Figure 59, the cyclic voltammograms at a pressure annealed pyrolytic graphite in 1M  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte with and without catalysts are shown. At a fresh and dry electrode surface, two reduction peaks are obtained without catalyst. With the addition of metal free phthalocyanine complex, the reduction peaks merged and peak current increased threefold. If monomeric cobalt phthalocyanine, CoPc, is added, the peak shifts to more positive potential. Furthermore, the cyclic voltammograms with catalysts do not contain reduction or oxidation peaks beyond 2.0 V.

Addition of  $\text{SO}_2$  to the electrolyte without catalyst generate a reduction peak at 2.0 V. However, with CoPc catalyst,  $\text{SO}_2$  reduction peak does not appear which could be due to the saturation of the electrode with adsorbed products. Similar results are also observed with the addition of  $\text{Cl}_2$ . Further studies are needed to identify peak positions of known additives and generate and identify species between 2 and -5 volt vs lithium reference electrode.

### FTIR

Studies on the nature of  $\text{SOCl}_2$  adsorption with carbon cathode with and without catalyst (CoPc or FePc) were initiated by FTIR spectroscopic techniques. Preliminary FTIR spectra (Figures 60-62) of  $\text{SOCl}_2$  with and without catalyst showed no significant variation in peak positions. The electrolyte thickness has to be minimized to study actual adsorbed layers. Further studies to optimize the FTIR cell design experimental conditions are needed.

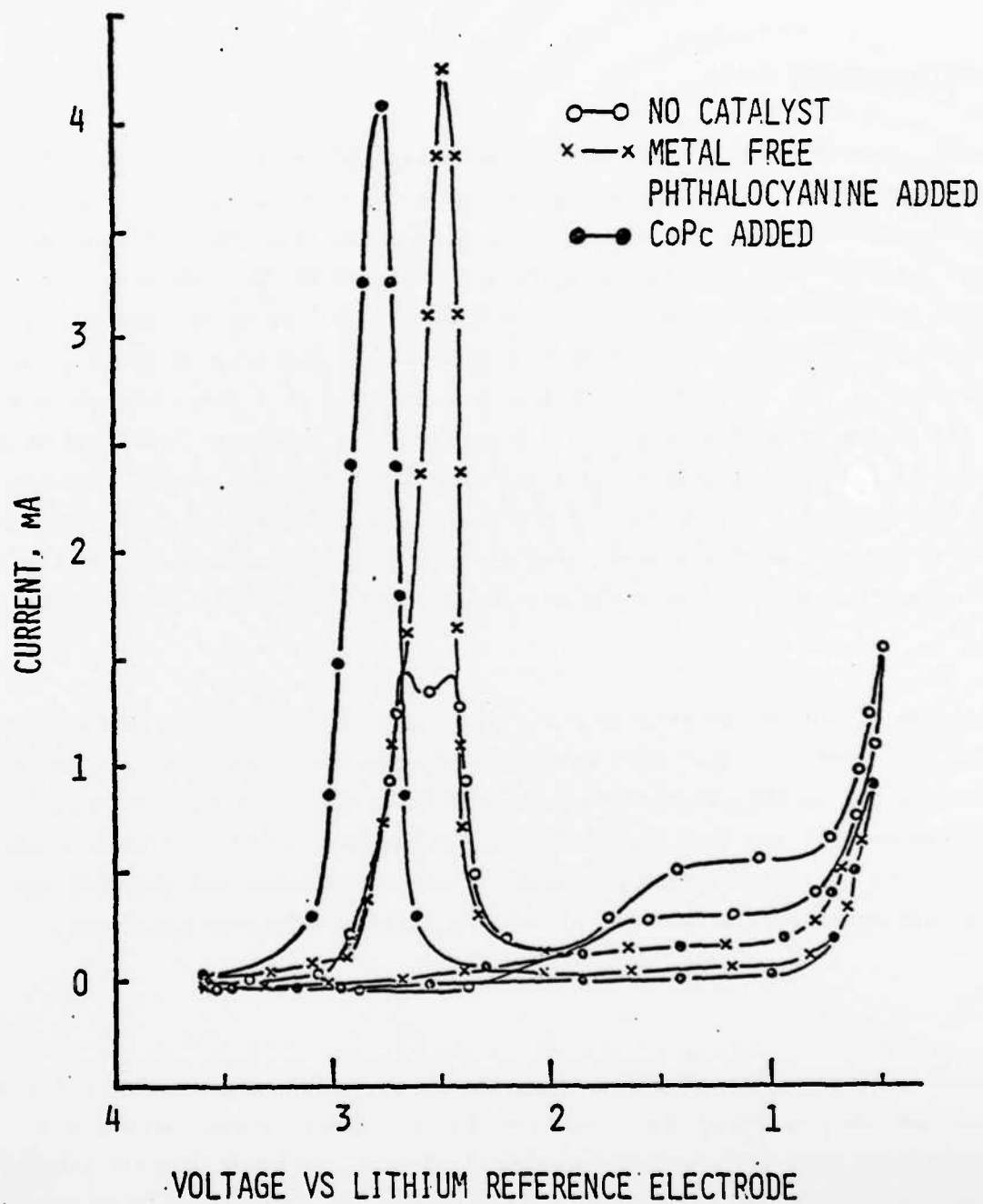


FIGURE 59. CYCLIC VOLTAMMOGRAMS AT PRESSURE ANNEALED PYROLYTIC GRAPHITE ( $0.178 \text{ cm}^2$ ) IN  $1\text{M LiAlCl}_4/\text{SOCl}_2$  ELECTROLYTE. SWEEP RATE  $100 \text{ mv/sec}$ .



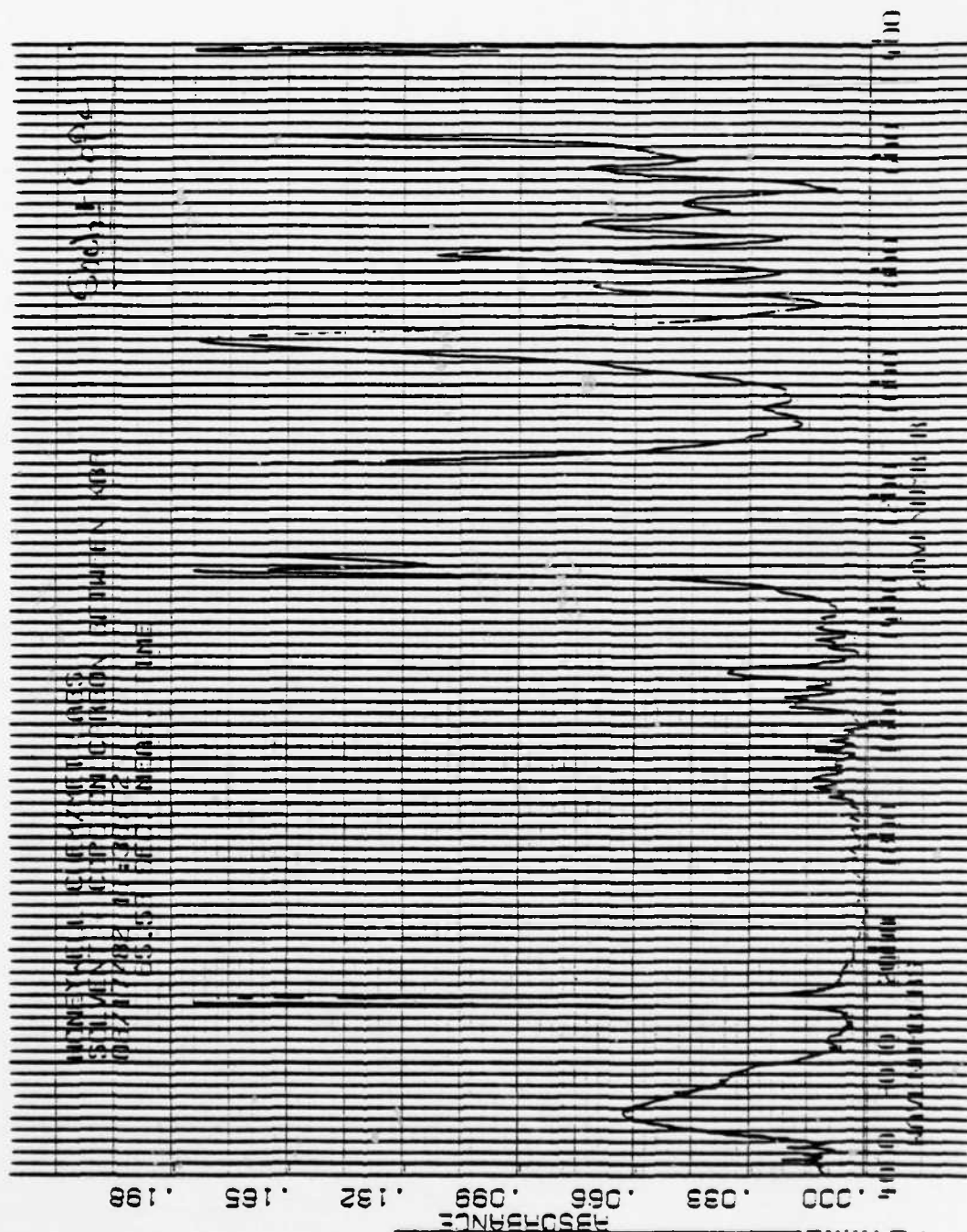


FIGURE 61. FTIR SPECTRUM OF  $\text{SOCl}_2 + \text{CoPc}$  ON POROUS CARBON CATHODES



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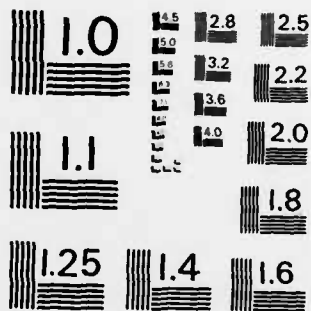
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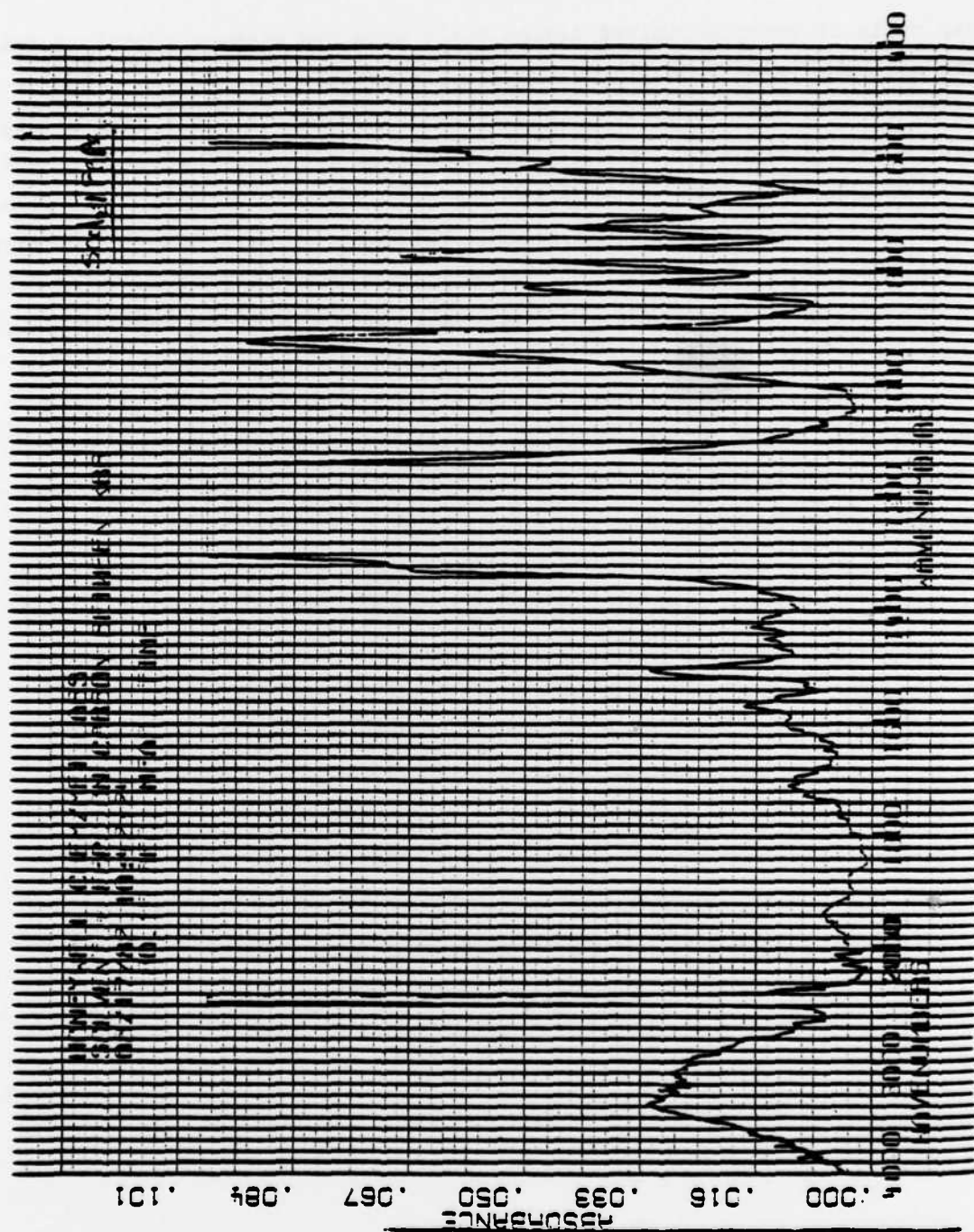


FIGURE 62. FTIR SPECTRUM OF  $\text{SOCl}_2 + \text{FePc}$  ON POROUS CARBON CATHODES

### Li/SO<sub>2</sub>Cl<sub>2</sub> SYSTEM

Wrap cells of cathode-limited design built with and without (CoPc)<sub>n</sub> catalyst, were activated with 1.5M LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> electrolyte in order to evaluate the effect on both performance and the safety of the system. The data of eight such cells are given in Table 8. The discharge cell life increases nearly by 20% over that of Li/SOCl<sub>2</sub>. However, the cells failed after only 65% of depth of forced overdischarge into reversal. The cause of cell failure was attributed to the electrical discontinuity. Postmortem of the cells showed both lead wires and anode grid were severely corroded. All cells exhibited pressure spike, temperature rise and voltage drop just before the cell failure. None of the cells, however, either exploded or vented. If stainless steel grids were replaced with nickel grids, the cell reversal time decreases further. Further studies are needed to identify the reactive species produced during reversal and the cause of grid corrosion.

Table 8. Discharge and Forced Overdischarge Characteristics of Li/SO<sub>2</sub>Cl<sub>2</sub> Cells with 1.5M LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> Electrolyte at 23°C

Serial No.	Cathode	Cell and Grid Type	Discharge Time (hrs) (1 mA/cm <sup>2</sup> ) (2.0V)	Pressure (psig) at 2.0V	Cell Reversal Time (hrs) (5 mA/cm <sup>2</sup> )	Pressure (psig) Just Before Cell Failure	Voltage (V) Just Before Cell Failure
1	Baseline	Wrap & S.S.	70	40	10.5	58	-0.2
2	Baseline	Wrap & S.S.	69	44	8.5	60	-0.2
3	(2) (CoPc) <sub>n</sub>	Wrap & S.S.	72	27	9.0	89	-0.2
4	(2) (CoPc) <sub>n</sub> + 0.5 g camphor	Wrap & S.S.	70	40	8.5	>200	0.2
5	(2) (CoPc) <sub>n</sub>	Wrap & Nickel	75	26	2.5	74	0.2
6	Baseline	Wrap & Nickel	74	28	-	-	-
7	(1) (CoPc) <sub>n</sub>	Wrap & S.S.	75	28	-	-	-
8	Baseline + CoPc 3 mg/cc	Wrap & Nickel	73.5	30	-	-	-

(1) Lithium was complete gone at the end of discharge time.

(2) Postmortem after overdischarge revealed severe grid corrosion; nickel grid was completely disintegrated, whereas the stainless steel grid became thinner (0.01" - 0.005"), also weld joints.

Notes: 1. Maximum temperature recorded at the time of cell failure was 150°F.

2. Pressure spike, temperature raise and voltage drop occur simultaneously.

3. Maximum cell pressure recorded was 110 psig.

## 6.0 SUMMARY AND CONCLUSIONS

- Temperature-pressure studies of D-cells showed:
  - No change in final pressure whether or not the cells were subjected to heat/cool cycles after various depths of discharges.
  - Maximum cell pressure at the end of 100% depth of discharge at 1 mA/cm<sup>2</sup> rate were 40 and 100 psig corresponding to 30 and 70°C operating temperatures, respectively.
- Long term reservoir storage studies revealed:
  - Stability of (CoPc)<sub>n</sub> in 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> electrolyte.
  - Surface corrosion on 316L and 321 stainless steel specimens.
  - Higher corrosion rates on 321 than on 316L.
  - Higher corrosion rates in acid electrolyte than neutral electrolytes.
  - Initial corrosion film inhibits or reduces further corrosion.
- Forced overdischarge into cell reversal studies showed:
  - (CoPc)<sub>n</sub> catalyzed cathodes improved cell voltages and did not show adverse effects on the behavior of cells during forced overdischarge.
  - Cathode-limited design cells sustained current densities up to 20 mA/cm<sup>2</sup> for 100% of nominal cell capacity during forced overdischarge into cell reversal. However, these cells showed unpredictable venting or exploding behavior, thus making them less attractive. Further, the current sustaining rate capability decreased when cells were built with lesser amounts of lithium. Based on the data of a few experiments carried out, it appears that balanced cells might be much more dangerous than cells having either anode-limited or cathode-limited design. In all cases, the cell failure appears to be related to thermal runaway conditions.



Anode-limited cells sustained higher current densities ( 20 mA/cm<sup>2</sup>) than cells of cathode-limited design. These cells experience severe heat generations leading to high cell pressures during cell reversal. However, none of the cells with optimized electrode stacks either vented or exploded. Reactive chemical species or lithium dendrites formed during discharge and forced overdischarge into cell reversal, if any, seemed to undergo changes leading to the formation of stable species at the high temperature environment in anode-limited design cells. Therefore, we believe that cells of anode-limited design are much safer under abuse conditions such as those described in NAVSEA's Instruction 9310.1A.

- Fundamental Studies

- Further electrochemical and non-electrochemical (FTIR) studies, with and without catalysts, are needed to identify the reactive species produced and the nature of SOCl<sub>2</sub> adsorption.

- Li/SO<sub>2</sub>Cl<sub>2</sub> System

- Li/SO<sub>2</sub>Cl<sub>2</sub> cells produced longer discharge life. Severe anode corrosion due to parasitic reactions was also observed during discharge.
- Future forced overdischarge into cell reversal, both nickel and stainless steel grids and lead wires, were severely corroded. Grid and lead wire corrosion appears to lead to the electrical discontinuity. During normal discharge, grid and lead wire corrosion was not observed. During studies are needed to understand the cause for the grid and lead wire corrosion.

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